TECHNOLOGY QUARTERLY

AND

PROCEEDINGS OF THE SOCIETY OF ARTS.

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PROCEEDINGS OF THE SOCIETY OF ARTS.

FORTY-FIRST YEAR, 1902–1903.

THE 575th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Friday evening, January 23d, at 8 o'clock, Professor Niles presiding. Eighty-five persons were present.

After the minutes of the previous meeting had been read and approved, Mr. F. H. Newell, Chief Engineer, United States Geological Survey, addressed the Society on "The Reclamation of the Arid Public Lands." The lecture was fully illustrated with lantern slides.

A vote of thanks was tendered the speaker and the meeting adjourned.

The 576th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, Thursday evening, February 12th, at 8 o'clock, Mr. James P. Munroe in the chair. Four hundred and fifty persons were present.

After the minutes of the previous meeting had been read and approved, Mr. George Kennan addressed the Society on "Martinique and Mt. Pelée."

A vote of thanks was tendered the speaker and the meeting adjourned.

The 577th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, February 26th, at 8 o'clock, Professor Cross in the chair. One hundred and twenty persons were present.

After the minutes of the previous meeting had been read and approved, Mr. George W. Miles, analytical and consulting chemist, was elected to Associate Membership in the Society.

The address of the evening was by Professor Louis Derr, who exhibited some new apparatus for illustrating certain electro-magnetic phenomena.

A vote of thanks was tendered the speaker and the meeting adjourned.

The 578th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, March 12th, at 8 o'clock, Mr. Peabody, of the Corporation, in the chair. Eighty-five persons were present.

After the minutes of the previous meeting had been read and approved, Mr. J. Knox Taylor, Supervising Architect, Treasury Department, addressed the Society on "Government Architecture."

A vote of thanks was tendered the speaker and the meeting adjourned.

The 579th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, March 26th, at 8 o'clock, Professor Talbot in the chair. Seventy-five persons were present.

After the minutes of the previous meeting were read and approved, Mr. H. J. W. Fay was elected to Associate Membership in the Society.

Mr. George W. Fuller then addressed the Society on "The Composition of Sewage with Relation to Problems of Disposal." The paper will be printed in full in the next number of the TECHNOLOGY QUARTERLY.

After the subject of the paper had been discussed by Professor Talbot, Professor Kinnicutt, and Professor Sedgwick, a vote of thanks was tendered the speaker and the meeting adjourned.

The 580th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, April 9th, at 8 o'clock, Mr. Munroe, of the Corporation, in the chair. One hundred and thirty-five persons were present.

After the minutes of the previous meeting had been read and approved, Mr. R. H. Dana addressed the Society on "The Charles River Dam." A number of lantern slides illustrating the subject were shown.

After a brief discussion, a vote of thanks was tendered the speaker and the meeting adjourned.

JAMES F. NORRIS, *Secretary.*

THE FIGURE OF THE EARTH FROM PENDULUM OBSERVATIONS MADE IN GREENLAND IN 1896 AND IN SUMATRA IN 1901 BY EXPEDITIONS FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

By G. L. HOSMER.

Ever since Richer, in 1672, observed the variation of gravity with the latitude, the pendulum has been recognized by geodesists as a valuable instrument for determining the figure of the earth. The recent improvements of the so-called "invariable pendulum" make this instrument more important than ever before as a means of solving this problem.

In 1743, Clairaut published his theorem for finding the flattening of the poles from the value of gravity at the equator and at the poles. His formula is:

$$\frac{a-b}{a} = \frac{5}{2} \cdot \frac{c}{g_e} - \frac{g_p - g_e}{g_e} \quad (1)$$

where a and b are the major and minor semi-axes of the meridian ellipse; c is the centrifugal force at equator; g_p and g_e are the accelerations due to gravity at poles and equator respectively.

It is not practicable to get the value of gravity at the pole directly, but, since the law of variation is known, we may reduce observations at any latitude to the corresponding values at the pole. The formula for this variation is:

$$g_o = g_e \left(1 + \frac{g_e - g_p}{g_e} \sin^2 \phi_o\right) \quad (2)$$

in which g_o is the value of gravity in latitude ϕ_o.

From this formula it will be seen that determinations of gravity at two different stations will give a value of $\frac{a-b}{a}$, or the polar compression. If many observations are taken, the most probable values

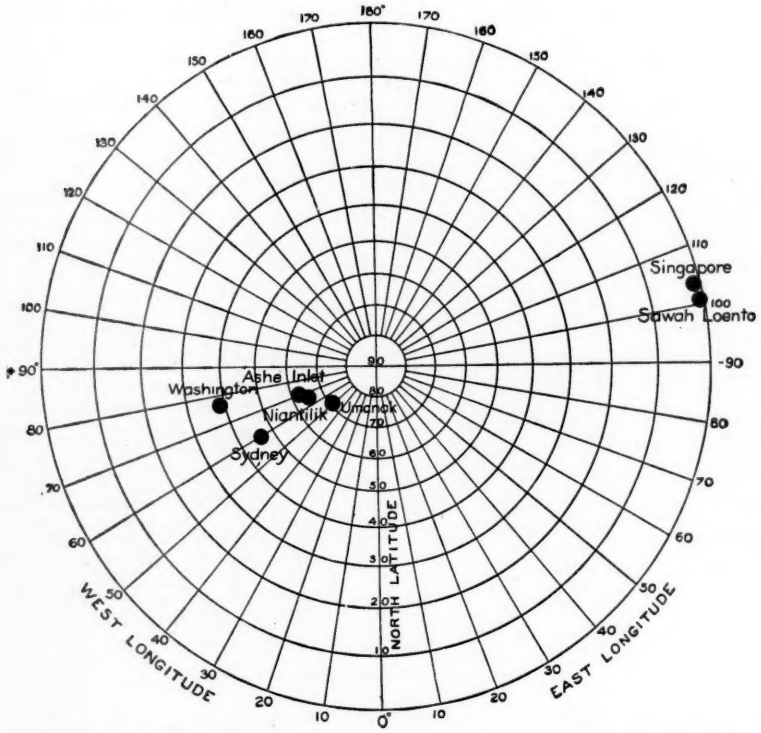
of g_e and g_p may be determined by the method of least squares and the value of $\frac{a-b}{a}$ may be found from these.

In this article we propose to derive a value for the polar compression depending upon observations for the force of gravity at the stations shown in the following table:

Station.	Observer.	Expedition.
Umanak, Greenland.	G. R. Putnam.	Boston party of sixth Peary expedition to Greenland, 1896, in charge of Prof. A. E. Burton.
Niantilik, Cumberland Sound.	G. R. Putnam.	Boston party of sixth Peary expedition to Greenland, 1896, in charge of Prof. A. E. Burton.
Ashe Inlet, Hudson Strait.	G. R. Putnam.	Boston party of sixth Peary expedition to Greenland, 1896, in charge of Prof. A. E. Burton.
Sydney, Cape Breton.	G. R. Putnam.	Boston party of sixth Peary expedition to Greenland, 1896, in charge of Prof. A. E. Burton.
Washington, D. C.	G. R. Putnam. G. L. Hosmer.	Reference station.
Singapore, Straits Settlements.	G. L. Hosmer.	Mass. Institute of Technology eclipse expedition to Sumatra, 1901, in charge of Prof. A. E. Burton
Sawah Loento, Sumatra.	G. L. Hosmer.	Mass. Institute of Technology eclipse expedition to Sumatra, 1901, in charge of Prof. A. E. Burton.

An inspection of the figure will show that these stations lie approximately along the same meridian. The measures of g were made with the half-second invariable pendulums belonging to the United States Coast and Geodetic Survey. This instrument gives the relative force of gravity at the points observed.

The values of g for the seven stations are shown in the following table. These values are based on the assumption that g at Washington is 980.102.



STEREOGRAPHIC PROJECTION OF NORTHERN HEMISPHERE SHOWING POSITIONS OF PENDULUM STATIONS.

STATION.	g REDUCED TO SEA-LEVEL.[1]	LATITUDE.	LONGITUDE.
Umanak.	982.595	+ 70° 40′ 29″	+ 52° 08′ 21″
Niantilik.	982.276	+ 64° 53′ 30″	+ 66° 19′ 32″
Ashe Inlet	982.111	+ 62° 32′ 48″	+ 70° 35′ 20″
Sydney.	980.723	+ 46° 08′ 32″	+ 60° 11′ 47″
Washington.	980.102	+ 38° 53′ 13″	+ 77° 00′ 32″
Singapore.	978.049	+ 01° 16′ 44″	— 103° 50′ 13″
Sawah Loento.	978.058	— 00° 41′ 40″	— 100° 46′ 40″

[1] For reports of these observations by the observers see Vol. X, p. 59, and Vol. XV, p. 35, of the TECHNOLOGY QUARTERLY and the Coast and Geodetic Survey Report for 1897, p. 299.

If we substitute in equation (2) for g_o the observed values, we obtain the following observation equations:

$$\begin{aligned}
982.595 - g_e - .890485\ (g_e - g_p) &= 0.\\
982.276 - g_e - .819943\ (g_e - g_p) &= 0.\\
982.111 - g_e - .787455\ (g_e - g_p) &= 0.\\
980.723 - g_e - .519930\ (g_e - g_p) &= 0.\\
980.102 - g_e - .394115\ (g_e - g_p) &= 0.\\
978.049 - g_e - .000498\ (g_e - g_p) &= 0.\\
978.058 - g_e - .000147\ (g_e - g_p) &= 0
\end{aligned}$$

$$\text{Assume } g_e = 978 + k$$

then the equations become

$$\begin{aligned}
4.595 - k - .890485\ (g_e - g_p) &= 0.\\
4.276 - k - .819943\ (g_e - g_p) &= 0.\\
4.111 - k - .787455\ (g_e - g_p) &= 0.\\
2.723 - k - .519930\ (g_e - g_p) &= 0.\\
2.102 - k - .394115\ (g_e - g_p) &= 0.\\
.049 - k - .000498\ (g_e - g_p) &= 0.\\
.058 - k - .000147\ (g_e - g_p) &= 0.
\end{aligned}$$

The normal equations are

$$\begin{aligned}
17.914 - 7k - 3.41257\ (g_e - g_p) &= 0.\\
13.07932 - 3.41257k - 2.51101\ (g_e - g_p) &= 0.
\end{aligned}$$

Hence $k = .0586$, $g_e = 978.059$ and $g_e - g_p = 5.1292$.
These values substituted in Clairaut's formula (equation 1) give:

$$\frac{a-b}{a} = \frac{5}{2} \cdot \frac{1}{288.41} - \frac{5.1292}{978.059} = \frac{1}{292.06}.$$

This value agrees closely with that given by Clarke in his work on geodesy, namely $\frac{1}{292.2}$. That a value derived from only seven observations should agree with one derived from a large number must be regarded as accidental, since the deviation of gravity at any station from the normal value may be considerable. The result indicates, however, that a few observations well distributed and all made with the same instrument, giving the relative force of gravity, will give a fair approximation to the true value.

A STUDY OF THE GEOLOGY OF THE CHARLES RIVER ESTUARY AND BOSTON HARBOR, WITH SPECIAL REFERENCE TO THE BUILDING OF THE PROPOSED DAM ACROSS THE TIDAL PORTION OF THE RIVER.[1]

By W. O. CROSBY.

Introduction.

The investigation was intended to cover the geological history of the present harbor and its channels, including the estuary of the Charles, in order to learn how far these channels had their origin in tidal scour, and how far the reported conclusions of forty years ago regarding the origin and preservation of the channels are in accord with the teachings of modern geology.

It was also desired that all recorded borings in the vicinity of the site of the proposed dam should be studied from the geological point of view, in order to learn the character of the ground on which the dam, with its heavy masonry locks and sluices, would have to be built.

The Bed Rock.

The geological data having a bearing upon the problems presented by the proposed dam across the tidal portion of the Charles River are chiefly those relating to the glacial and postglacial periods in the history of the river. The underlying bed rock, largely of a slaty character, is in general, and especially for points near the modern river, so deeply buried beneath the glacial and later deposits as to be without appreciable direct influence in determining surface features and conditions. Under the general processes of glacial and preglacial erosion, however,

[1] This study, printed with permission of the Charles River Dam Committee, was made in order to answer certain questions propounded by J. R. Freeman, Engineer to the Committee, with special reference to the probable effect of the proposed dam near Craigie Bridge upon the shoaling of the harbor, and also in order to learn the character of the deep substrata at the proposed dam site in relation to furnishing an impervious and unyielding foundation for the dam, the locks, and the sluices

the character and structure of the bed rock have undoubtedly determined in a large degree the contours and trend of the bed-rock valley; but these are reflected in the surface topography only in a very broad and general fashion, and chiefly indirectly, determining the accumulation or massing of the glacial drift or bowlder clay in which the relief features of this part of the valley are now mainly expressed. It appears, therefore, that, notwithstanding its unobtrusive character, the bed rock is still a factor in this problem, and the natural starting-point of the investigation.

Character and Structure of the Bed Rock.

Many borings and excavations, supplemented by an occasional outcrop toward the head of the estuary, suffice to show that the concealed bed-rock floor of this part of the Charles River valley is mainly slate, of similar character to that so well exposed in the Somerville ledges and quarries, with probably, as in Somerville, an occasional dike of diabase (trap).

The general geologic structure of this district is comparatively simple. The main features, beginning on the south, are:

First. — A broad band of conglomerate, trending east-west through Newton, Brookline, Roxbury, and Dorchester to the harbor at Savin Hill. The structure of this belt of conglomerate is anticlinal, the beds dipping northward on the north side and southward on the south side, and passing in both directions beneath the overlying slate formation, which once arched completely over and concealed the conglomerate. Not only has erosion cut through the slate and deeply into the conglomerate, but to the westward, in Newton and Needham, it has also cut entirely through the conglomerate, exposing the ancient volcanic rocks — melaphyr and felsite — which here form the floor of the Boston basin. As it approaches the sea this broad arch of conglomerate narrows rapidly, the axis subsiding in this direction; but it probably extends at least as far east as Thompson's Island before it is completely covered by the slate. This anticlinal belt of conglomerate lies about midway between the northern and southern borders of the Boston basin — the northern highlands (culminating in Arlington Heights) and the Blue Hills, — and is at once the central and dominant arch or structural feature of the basin, determining, by its superior resistance to erosion as compared with the softer bordering slates, a topographic division of

the basin into two broad longitudinal valleys — the Charles and the Neponset.

Second. — Each of these main valleys is divided longitudinally by a subordinate belt of conglomerate and volcanic rock. That on the north, in which alone we are now interested, extends through Newton and Brighton, south of the Boston & Albany Railroad, but seems to die out in Brookline before reaching the Back Bay district of Boston, the belt of slate separating it from the main central belt of conglomerate widening rapidly eastward from the vicinity of Chestnut Hill Reservoir.

Third. — In the hills north of the Charles River, in Watertown, another, but very subordinate, anticlinal ridge of conglomerate rises through the slate. But with this exception, the entire area between the conglomerate of the Newton and Brighton ridge and the granitic rocks of the northern highlands, expanding eastward to embrace Belmont, Cambridge and Somerville, is underlain, so far as known, by slate, which, in the longitude of Boston proper, is probably continuous from Arlington Heights to the northern boundary of Dorchester and the southern shores of South Bay and Old Harbor.

Fourth. — Below Riverside the course of the Charles River is wholly confined to the southern part of the broad, northern slate area, where the structure is clearly synclinal, the topographic valley coinciding with a geologic valley. The trend of this slate syncline, conforming with the Newton and Brighton anticline, is first to the north-northeast, parallel with the western border of the basin, nearly to Waltham, and then to the eastward, as far as Cambridgeport and the eastern end of the anticline, where, probably, it is deflected toward a southeasterly course in conformity with the ledges of Somerville and Governor's Island. Having once reached this trough of relatively soft rocks, the river has followed it to the sea, and continues to follow it, with some obvious meanders and digressions, in spite of the deep drift deposits which now encumber and obscure its bed-rock valley.

Topography of the Bed Rock.

The genera. conclusions to be noted under this head are mainly based upon, first, the actual outcrops of the bed rock; second, the drumlins or special accumulations of bowlder clay, which are usually either based upon ledges or indicate relatively elevated portions of the bed-rock surface, and embrace nearly all the bowlder clay of this area

not covered by modified (washed and stratified) drift; and, third, and especially, upon all the deep borings and excavations of which I have been able to obtain a definite record.

It may be noted not only that the distribution of the drumlins is in harmony with that of the rock outcrops, the two classes of facts co-operating to determine the outline of the bed-rock valleys; but also that the bed-rock contours, based chiefly, as stated, upon the borings, are yet in harmony with both the natural outcrops and the drumlins.

We thus discover not only that the bed-rock valley of the Charles River follows approximately the modern course of that stream below Riverside, and that both are in substantial harmony with the geologic structure; but also that it is joined, between Brighton and Cambridge, by a still deeper and broader valley from the northward, which is readily identified as a direct southward continuation of the valley of the Mystic River where it cuts through the northern highlands and enters the Boston basin.

The highland section of the valley of the Mystic is, in size, out of all proportion to the diminutive stream which now poses as its architect; and, as I have elsewhere shown,[1] it is highly probable that we have here the preglacial channel of the Merrimac River, which followed the general course of the Middlesex canal from the great bend at North Chelmsford to West Medford, whence, instead of bending abruptly to the eastward, as does the modern Mystic, it continued in the same general direction across Cambridge to its confluence with the Charles, this part of its course being approximately marked now by the basins of Spy and Fresh ponds, and being further attested by the deep boring near the outlet of Fresh Pond, which reached bed rock at a depth of 148 feet, or about 130 feet below mean sea level.

The Charles thus appears as a preglacial western tributary of the preglacial Merrimac; and the course of the united streams, or of the Merrimac after receiving the waters of the Charles, was clearly not that of the modern Charles around the north end of Boston, but directly across the Back Bay and the South End districts of Boston (Boston Neck and Dorchester Neck) to Old Harbor.

It is extremely probable, as will appear more clearly later, that the slate ledges of Somerville are continued as more or less distinct

[1] Technology Quarterly, Vol. XII, p. 302.

ridges underlying Charlestown and the north end of Boston. These ridges are doubtless more or less irregular and discontinuous; but there seems to be no reason to doubt that they should be regarded as an effectual bar to the view that the preglacial drainage of the Charles River valley followed the course of the modern river below Harvard Bridge.

On the other hand, the far more direct southern course is free and unobstructed to a depth of 200 feet or more. The southern border of this valley is quite well defined by the outcropping ledges in Brighton, Roxbury, and Dorchester, and the northern border is also indicated by less prominent ledges in South Boston. Reviewing the borings, we find that beneath Cambridgeport the bed rock is from 110 to at least 150 feet below sea level, rising toward the north; across the Back Bay and South End districts of Boston, several borings have reached the bed rock at depths of 140 to 170, and even 200 feet; and a boring near the northern shore of the Calf Pasture in Dorchester, and presumably on the southern slope of the valley, reached bed rock at a depth of 166 feet; while at the pumping station of the main drainage system, at Old Harbor Point, bed rock was reached at a depth of 214 feet, or 204 feet below low tide. It is apparent that from West Medford the preglacial Merrimac held its southward course across the Boston basin until it was joined by the Charles near the east end of the Newton and Brighton anticlinal band of the harder rocks; and that from this point the course was more southeasterly, but still crossing the strike of the slate beds, until it met the north side of the great Brookline and Savin Hill arch of conglomerate, which deflected it to the eastward, the seaward course of the buried channel being probably to the north of Thompson's and Spectacle islands, and thence seaward *via* Presidents Roads and Broad Sound.[1]

Continuing the general view of the bed-rock topography and recalling that the normal bed rock for the entire district north of the highlands is slate similar to that of the Somerville ledges, we may note: first, that the prevailing strike of the slate, so far as determined, varies from approximately east-west near the Charles River to about northwest-southeast in the vicinity of the Mystic; and, second, that the slate, more or less steeply inclined at most points, naturally

[1] This problem of the preglacial course of the Charles River has been ably discussed by Mr. F. G. Clapp, TECHNOLOGY QUARTERLY, Vol. XIV, p. 198.

tends to form ridges trending with the strike, with, of course, intervening valleys, which must in general slope seaward. This is confirmed by all the outcrops and all the borings which have reached solid bed rock. It may also be assumed that all parts of the bed-rock surface would, if bare and elevated above sea level, exhibit free drainage; in other words, that there are in this district no true rock basins.

One of the longest and most pronounced of the bed-rock ridges is indicated by the drumlins of College and Winter hills and the ledges on which they rest, Convent Hill (recently removed), Bunker and Breed's hills in Charlestown, Man-of-War Shoal (summit of a submerged drumlin), the low drumlin culminating in Maverick Square, East Boston, and the more prominent East Division drumlin, Bird Island flats (another submerged drumlin), Governor's Island drumlin and ledge, and the flats extending a mile beyond. It is a fair assumption that a ridge of this length is composite, consisting of overlapping and more or less distinct members; and probably the lowest point is between Charlestown and East Boston, this *col* descending, possibly, 100 feet below low tide and marking the head of a valley descending to the south, between Boston and East Boston. Whether simple or complex, this ridge is clearly the southern slope or wall of a deep main valley, following the present course of the Mystic below West Medford, and the product especially of the drainage of the Malden and Melrose valley. The deep borings on the north side of Charlestown, reaching depths of — 100 to — 120 feet,[1] are doubtless in this valley, but south of its axis; while the Chelsea Ferry boring, reaching the ledge at about — 65, is well up on the north slope and this is confirmed by the Government Hill drumlin; and that the true course of the valley is directly east from the mouth of the Mystic, across East Boston in the vicinity of Central Square, south of Eagle Hill, is indicated by the geological structure, and suggested by a boring which failed to reach bed rock at a depth of — 100 feet on the flats between the First Division drumlin and the small drumlin of Wood Island Park. This course continued leads to a confluence with the Merrimac-Charles valley between Deer Island and Long Island.

[1] From this point on, depths and elevations are referred to Boston base or approximate low tide.

The ledge later to be described as underlying the Warren Bridge and Copp's Hill may apparently be regarded as a southern branch of the ridge just described, or, perhaps better, as a minor ridge between this and a second main ridge including, besides the ledges of Clarendon and Powder House hills, the drumlins of Spring, Central, Prospect and Asylum hills in Somerville, East Cambridge Hill, Beacon and Fort hills in Boston and the Burnham Channel ledge. The East Somerville drumlin tends to connect these two linear series of hills; and, while to the northwest of this point the ancient drainage may have been tributary, laterally through the first ridge, to the valley of Malden River, to the southeastward it was quite certainly longitudinal, passing beneath the present bed of the Charles River between the Lowell and Warren bridges, as will be more fully shown in a later section, and thence eastward between Beacon and Copp's hills and north of Fort Hill. Some idea of the depth of this part of the valley is afforded by the fact that bed rock was not reached at —115 feet at the corner of State and Broad streets, and only at a depth of —135 feet close on the northeast side of Fort Hill. Farther east, confluence with the minor valley heading in the neighborhood of the Man-of-War Shoal appears probable, and the course is indicated by a boring with a record of —118 feet and no rock at Pier 4, South Boston. Beyond this the course is open to doubt, but is probably north of the Burnham Channel ledge and south of Castle Island to a confluence with the Merrimac-Charles valley between Castle and Thompson's islands.

The drumlins of North Cambridge suggest, in connection with the Spring Hill and Winter Hill drumlins and their associate ledges in Somerville, a transverse ridge or water parting; and from the southwestern end of this ridge a third northwest-southeast ridge extends at least as far as the city hall, the slate bed rock on this line having been well exposed in sewer excavations in the yard of Harvard College, and almost continuously southward to the river. Between this area of a relatively high bed-rock surface and the ledges and drumlins of Somerville is apparently a broad valley, the drainage of which, as indicated by the low level reached by the bed-rock surface in several borings in the lower part of Cambridgeport, probably escaped to the southward to become immediately tributary to the Merrimac-Charles valley.

Only one other bed-rock ridge remains to be mentioned. This

embraces the drumlins and ledges of South Boston, including the Half-tide Rock; and with greatly diminished height it appears to be continued westward under South Bay and the South End into the heart of the Back Bay district. The borings indicate that west of South Bay the elevation of the crest of the ridge varies between —60 and —80 feet to its abrupt termination.

North of this deeply buried western half of the South Boston ridge, between it and the high Beacon Hill section of the Somerville and Boston ridge, is a broad, deep valley, the axis of which is at least 160, and probably 200, feet or more below the Boston base. The anomalous feature of this valley is that, while it appears to merge broadly with the Merrimac-Charles valley on the west, it is, for the lower levels, closed to the eastward. It appears thus as a short, broad, deep, *retrograde* tributary of the main drainage channel of the region.

In seeking an explanation of this depression, we may profitably note the fact that some of the borings reporting bed rock in the section of Boston south and east of Beacon Hill have clearly not reached any of the hard and thoroughly solid rocks (slate, conglomerate, trap, etc.) such as make up the whole of the bed-rock surface wherever it is exposed in ledges and shallow excavations; but instead the drill has passed from the glacial drift to imperfectly consolidated sands, clays, marls, etc., in part of colors unknown to the drift, and probably representing Tertiary strata underlying the drift and filling deep depressions or valleys in the harder formations or true bed rocks of the region. The artesian well of N. Ward & Co., on Spectacle Island, 560 feet deep, passed through at least 360 feet of unconsolidated material, only part of which could be regarded as glacial drift; and the deep well at the corner of High and Purchase streets in Boston, reported as reaching the bottom of the drift at about 100 feet, is in soft materials comparable with the Tertiary deposits of Martha's Vineyard and Long Island, to a depth of at least 500 feet. Following up this idea, it is a natural suggestion that during the strong elevation of the land at the close of Cretaceous time the Merrimac-Charles River, then flowing directly eastward south of Beacon Hill and Fort Point Channel, cut a deep valley in the ancient bed rocks of the region; and then during the Tertiary subsidence the lower portion at least of this valley was filled by Tertiary strata, and thus virtually obliterated; and the stream, during the succeeding ele-

vation, chose a new course across the horizontal Tertiary plain, and parallel with the great conglomerate anticline, where during the Pleistocene (early glacial) elevation it again trenched the older bed rocks, this channel being in turn obliterated by the deposits of the glacial period; and the river, in obedience to merely fortuitous or accidental causes, adopted its present circuitous course around the north end of Boston. It would thus appear that the channel was originally directly across the city proper (Cretaceous time), and that in the later history of the river it was diverted first to the south (Tertiary and Pleistocene times) and then to the north (postglacial time).

According to this view, the anomalous retrograde bed-rock valley south of Beacon Hill is the original channel partially re-excavated during the early Pleïstocene elevation of the land.

Normal Profile of the Bed-Rock Channel, and Its Relations to the Early Glacial History of the Region.

For one important feature of the bed-rock topography we are not directly dependent upon either surface observations or borings, since it is a universal feature of the major valleys of the glaciated zone, and, in a general way at least, may safely be inferred where the data fall short of a complete demonstration. The feature referred to is an inner gorge, trenching the floor of the main valley and extending into the principal tributary valleys. This gorge is in this region rather seldom indicated in the surface topography, being almost universally filled by drift deposits, and thus obliterated as a topographic feature. It has been fully demonstrated for the valley of the Nashua River by the numerous deep borings made by the Metropolitan Water Board in the vicinity of Clinton, revealing a narrow gorge some 200 feet deep, dividing the bed-rock floor of this broad valley.[1] It is demonstrated also for the valley of the Merrimac by the deep borings of the Lowell water works, between Lowell and North Chelmsford, the gorge in this instance being about 100 feet deep, and its bottom at or below sea level; and also by the deep basin of the lower Mystic Lake, the water in which has a depth of 75 feet, and probably overlies a very considerable depth of drift.[2] Similar facts have been observed for many other streams; and the gorges of the larger rivers may be traced seaward for many miles,

[1] Technology Quarterly, Vol. XII, p. 294.

[2] Technology Quarterly, Vol. XII, p. 300.

the gorge or submerged fiord of the Hudson having still an unfilled depth below sea bottom, as determined by soundings, of over 2,800 feet, 80 miles east of Sandy Hook.

We find the simple and sufficient, and apparently the only possible, explanation of these phenomena in a strong elevation of the land at the beginning of the great ice age; this elevation, which amounted in this latitude to at least 3,000 feet, being regarded by many glacialists as the chief cause of the continental glaciation. This continental uplift must have proved a great stimulus to the drainage, especially near the continental border; and the streams, as their fall and erosive power increased, must in general have ceased meandering and thus slowly widening their valleys, and begun to cut rapidly downward toward a new base level. Thus were developed, before the land was finally covered by the great ice sheet, a system of deep, U-shaped gorges, trenching the floors of the relatively broad and shallow preglacial valleys.

In this vicinity the borings are insufficient to define the gorges of the Charles and Merrimac valleys; and it is at least among the possibilities that no borings have been located on the deepest lines or axes of the broad valleys. Of the existence of a deep inner valley there can, however, be no question. A well-defined lateral gorge is clearly indicated by the borings in the valley of Stony Brook, where it cuts through the Roxbury highlands. To this inner valley or gorge and its tributaries the floor of the preglacial valley stands in the relation of a terrace; but the borings appear inadequate at most points to determine satisfactorily the normal elevation of this terrace. In the Back Bay and South End districts, however, or just where the surface features count for the least in locating the gorge and determining the breadth and elevation of the bed-rock terrace, the borings do help us out to some extent, showing the general floor of the preglacial valley to be at least 60 feet below mean sea level.

Bed-Rock Details for the Charles River Below Harvard Bridge.

The modern course of the Charles below the Harvard Bridge is not only unnaturally circuitous, but the depths of the bed-rock surfaces are in part much less than at points farther up stream. The evidence may be briefly summarized here: —

The 39 borings on the line of the Harvard Bridge to depths ranging from —31.4 to —77.7 feet failed in every instance to reach bed rock, the entire series ending in blue clay. The deepest boring, —77.7 feet, is 100 feet from the Boston end of the bridge.

The borings for the new West Boston Bridge, 64 in number, on three different lines, and varying in depth from —36.9 feet to —73.5 feet, also failed in every instance to reach bed rock. Three borings, —46.4, —46 and —51.6 feet, struck rock, marked on the profiles "stone, probably bowlder," and this interpretation is probably correct. It may be added, however, that all of these borings ended in bowlder clay, indicating that the bed rock is less deep than at the Harvard Bridge.

No borings are available for the Craigie Bridge, but for the first bridge of the Boston & Lowell Railroad, built in 1833, we have a full series. This bridge, which is now used for freight tracks of the Boston & Maine Railroad, crosses the river somewhat diagonally, at a mean distance of about 250 feet below the Craigie Bridge. The borings, numbering 133, in two lines, the southern line being most complete, range in depth from —12 to —45.4 feet; and with a very few exceptions they all end on or in bowlder clay, although apparently no serious attempt was made to penetrate the bowlder clay or hard pan. At the Boston end of the bridge several borings in each line reached slate bed rock at depths varying from 12 to 17 feet below low tide, the depth increasing westward.

No boring data for the other railroad bridges have come to light; but for the Warren Bridge we have a series of 10 borings, extending across the river; and with two exceptions they all reach bed rock, at depths ranging from —11.84 to —39.68 feet.

Of the 70 borings made for the new Charlestown Bridge, on three different lines and to depths ranging from +4.3 feet to —58.3 feet, the deeper borings being mainly toward the Boston side of the river, only one is reported as reaching ledge, and this at a depth of only —11 feet in Charlestown. Another boring, 175 feet nearer City Square, is marked as ending on a bowlder at a depth of —5.7 feet, and it appears highly probable that this interpretation should be applied in both cases. This appears the more necessary, since, with the exception of two borings near the Boston end of the bridge which end in blue clay, they all end in bowlder clay.

Of 55 borings made for the new dry dock at the Charlestown

Navy Yard, in an area 1,300 by 700 feet, and reaching depths ranging from —33 to —104.4 feet, nine reached slate bed rock at depths varying from —39 to —98, and penetrated it 0 to 14.4 feet. A comparison of these bed-rock determinations shows that they partially outline a valley deepening in a northeasterly direction.

These several series of borings clearly indicate a bed-rock ridge crossing the river, the crest of the ridge being on or near the line of the Warren Bridge. Apparently the only alternative is to assume that, in the case of each of the Warren Bridge borings reported as ending on rock, the rock was a bowlder, and not ledge. But, even then, such frequency of bowlders large enough to be mistaken for ledge would suggest the close proximity of the ledge.

In East Cambridge and Charlestown bed-rock determinations, besides those already mentioned, are few, and none are very shallow. Two or more wells of J. P. Squire & Son on Gore Street, East Cambridge, reached bed rock at about —45 feet; a well of the Charlestown Gas Company at Thompson Square encountered bed rock at the same depth; and it was found at a depth of —59 feet in the well of G. G. Fox, Edgeworth and Vine streets, Charlestown. Although not very shallow, these borings are clearly not deep enough to suggest their location in or near the preglacial channel of the Charles; and it may quite safely be assumed that the drumlins of East Cambridge, Asylum Hill, Breed's Hill, and Bunker Hill rest on still more elevated portions of the bed-rock surface.

On the Boston side of the river borings and bed-rock determinations are much more numerous, and sufficient to develop, at least approximately, the form of the bed-rock surface. Starting from the Boston end of the old Boston & Lowell Railroad Bridge, where, as already noted, slate bed rock was reached at depths ranging from —12 to —17 feet, we find that the bed-rock surface rises southward, toward the low ridge or drumlin crossed by Leverett and Chambers streets, and that it formerly reached the level of low tide at the corner of Brighton and Lowell streets.

The borings made for the Charles River embankment, extending from Leverett Street and the Craigie Bridge to Cambridge Street and the West Boston Bridge, along the front of the wall, and to the number of 50, ranging in depth from —0.8 to —63 feet, discovered bed rock at 32 points, between 200 and 950 feet south of Craigie Bridge, at depths varying from —0.8 to —44.6 feet. These bed-

rock determinations are so grouped as to indicate a rather flat-topped ridge, from 1 to 8 feet below low tide, with fairly steep lateral slopes; clearly a northwestward continuation of the ridge on which the Chambers Street drumlin is built, and probably continuous under the river with the bed-rock elevation bearing the East Cambridge drumlin.

On Charles Street, about 200 feet east of the embankment line of borings, we have a nearly parallel profile in the 22 borings, 0 to — 33 feet in depth, made for the new sewer between Leverett and Cambridge streets. Of this series, 10 borings reached bed rock at depths of 0 to — 13 feet within a distance of 800 feet south from Leverett Street; and continuing through Leverett and Brighton streets to Lowell Street we find 7 borings, all of which reach bed rock at depths from + 8 to — 10 feet. A comparison of the profiles shows the average elevation of the bed rock to be increasing eastward, although the ridge is divided on Charles Street by a valley at least 15 feet deep.

That this ridge continues to the eastward we have abundant evidence in the fact that the sewers have also encountered ledge (slate) on Poplar Street and Kennard Avenue, and that the following houses stand on slate ledge, at elevations ranging from + 15 to at least + 25: Nos. 33 and 67 Poplar Street, corner of Poplar and Spring streets, corner of Milton and Spring streets, and corner of Poplar Street and Kennard Avenue. The general course of this ridge is southeasterly, with the axis of the drumlin, as shown by bed-rock elevations of — 15 feet in the wells of Fobes, Hayward & Co., on Chardon Street, and Graves & Sons, Bowker Street; — 50 feet at Marston's Restaurant, on Hanover Street; — 28 feet at Pemberton Building, Pemberton Square; and — 15 feet, corner of Washington and Court streets. The narrowness of the ridge is proved by a bed-rock elevation of — 15 feet in the artesian well of the Massachusetts General Hospital, near the corner of Allen and Blossom streets.

Following the profile of the Charles Street borings southward, around the base of the main drumlin of Beacon Hill, we have 14 borings, ranging from about + 1 to — 14 feet in depth. Of these, 4 reached the slate bed rock in the vicinity of Pinckney Street, on the axis of the drumlin, at depths near the low-tide level (+ 1 to — 2), and two others, between Mt. Vernon and Chestnut streets, at depths of — 10 and — 14 feet, approximately.

The broad valley between Beacon Hill and its dependent drumlins

and the relatively small but well-defined drumlin of Copp's Hill corresponds to a bed-rock valley. Of this we have abundant evidence. Thus, of the 15 borings for the new sewer, on Causeway Street between Lowell and Prince streets, reaching depths of +8 to −36 feet, only those at the intersections of Charlestown and Prince streets, and possibly only the latter, reached bed rock, at elevations of +1 to +8 feet. All the other borings of this series terminated in blue clay or sand, not one of them even reaching the bowlder clay, which presumably covers the bed rock in the valleys, as well as on the ridges, though less thickly. In close proximity to the Prince Street boring is the deep artesian well of the Boston Gas Company, in which slate bed rock was reached at −35 feet. The bed-rock elevation proved by the borings is probably an eastward extension of the bed-rock ridge disclosed by the Warren Bridge borings, and it may be assumed to continue as the axis or foundation of Copp's Hill. Between Copp's Hill and Beacon Hill we have the following additional bed-rock elevations, afforded by artesian wells and borings, and proving the existence of a bed-rock valley at least 75 feet deep below Boston base: Moxie Nerve Food Company, Haverhill Street, −53 feet; Schrafft & Sons, Portland Street, −65 feet; Tufts old factory, Portland Street, −49 and −74 feet; Eastern Cold Storage Company, 28–44 North Street, −104 feet; Boston subway borings, between Causeway and Hanover streets, −5 to −40 feet, in clay and no rock.

The Bowlder Clay and Drumlins.

The bowlder clay, or hard pan, known by geologists also as the till or ground moraine, is the unmodified (unwashed and unstratified) portion of the glacial drift, or that part of the drift deposited on the final melting of the ice sheet without being exposed to the effective sorting or modifying action of water. It rests at most points directly upon the bed rock, and in this region at least is found chiefly on the higher parts of the bed-rock surface, where it is very largely massed in the form of rounded hills or drumlins. The practical exclusion of the bowlder clay from the deeper valleys is a fact of great significance and interest, indicating that the ice continued to move along these lines after it had become stagnant on the uplands, and suggesting comparison with a river, the chief deposits of which are not on its bed but on its flood plain.

As regards its relations to the subterranean movement of water and the stability of foundations built upon it, the bowlder clay, having been compacted by the tremendous and long-continued pressure of the ice sheet, is comparable with the underlying bed rock; and in this connection it is interesting to note the concentration of bowlder clay in the vicinity of, and below the site of, the proposed dam, as indicated by the drumlins and numerous borings. The main facts are clearly and instructively exhibited in a direct comparison of the borings.

Thus, beginning on the southwest, or over the main bed-rock valley, we find that none of the Harvard Bridge borings encountered the bowlder clay; although the minimum elevation reached by the borings is —77.7 feet, they all ended in blue clay, which overlies the bowlder clay. Of the numerous borings for the West Boston Bridge, all reached bowlder clay at elevations ranging from —29.4 feet at the Boston end of the bridge, where the slope of the Beacon Hill drumlin passes beneath the river, to —66.1 feet at a point 300 feet farther west. From the axis of this bowlder clay valley, which is indicated on each of the three lines of borings, and slopes northward from —57.5 feet on the south line of borings to —66.1 feet on the north line, or approximately 10 feet in 100, the surface of the bowlder clay rises westward to elevations between —40 and —30 in about 300 feet, beyond which it falls off to about —50 in the next 400 to 500 feet, and then continues with a slightly undulating surface but no decided or general slopes for fully 1,000 feet, or to the Cambridge shore, where the elevations on the different lines are, from south to north, —55.35, —50.5 and —49.3 feet. This approximately plane upper surface of the bowlder clay is undoubtedly very characteristic of the interdrumlin areas, and probably indicative of a similar flat bed-rock surface below a moderate thickness of bowlder clay.

The Charles River embankment borings, although extending across the axis of the northern spur or member of the Beacon Hill drumlin, and ranging in depth to a maximum of —63 feet (midway between the West Boston and Craigie bridges), have all failed to reach the bowlder clay, showing apparently that the valley in the bowlder clay developed by the West Boston Bridge borings continues under the eastern margin of the river at least as far as Craigie Bridge, and probably continues to deepen in that direction, since it is improbable that the embankment borings are near the axis of this trough.

The Charles Street sewer borings, following more closely the base of the drumlin, have found the bowlder clay at or near the surface at nearly all points between Beacon and Cambridge streets, although it is difficult here to distinguish original deposit from artificial filling; but between Cambridge and Leverett streets, where most of the borings not ending on the high level bed rock attained depths of — 25 to — 33 feet, none have encountered typical bowlder clay, developing chiefly clay of a more or less sandy character.

The numerous borings of the original Boston & Lowell Railroad Bridge reached the bowlder clay in most cases, and at depths averaging much less than for the West Boston Bridge borings, although again we note a surprising uniformity of depth for the main part of the profile. For the first 300 feet from the East Cambridge shore the borings were too shallow (— 17 to — 23 feet) to reach the bowlder clay; but for the next 250 feet it is developed at depths ranging from — 23 to — 33 feet. In the next 250 feet depths of — 40 to — 45 have ended in blue clay, marking the position of the deep channel in the bowlder clay with depths of the bowlder clay surface probably exceeding 70 feet, if the valley continues to deepen northward. This locates the bowlder clay channel near the middle of the river at this point; and east of the channel the bowlder clay shows again a striking uniformity of elevation, ranging only from — 31 feet to — 35, for fully 800 feet, or to the slate ledge on which the east end of the bridge rests.

On the line of the Warren Bridge two borings, 275 and 280 feet from Causeway Street, reported bowlder clay at depths of — 16.3 and — 27.6 feet, and 670 feet from Causeway Street at — 33.3 feet. These are clearly on the northwestern slope or toe of the Copp's Hill drumlin. At 918 feet from Causeway Street bowlder clay is wanting, and rock was reached at — 11.8 feet. The next boring, 1,118 feet from Causeway Street and 696 feet from Water Street in Charlestown, ends in gravel at — 16 feet, and the next, 576 feet from Water Street, in clay and stones (probably bowlder clay) at — 32.2 feet. Beyond this we have, at 490 feet from Water Street, rock at — 32.2 feet and no bowlder clay; and at 264 and 190 feet, respectively, from Water Street, rock at — 12 and — 15 feet, and no bowlder clay. These facts seem to prove the existence, between the Copp's Hill and Beacon Hill drumlins on one side and the Charlestown drumlins on the other, of a ledgy tract, essentially bare of drift,

as is so commonly observed between well-developed drumlins above sea level; and it appears improbable that the valley in the bowlder clay, traced from the West Boston to the Craigie Bridge, finds an outlet in this direction, but, if continued, it is more likely to turn to the eastward, between Beacon and Copp's hills. It is, however, quite unnecessary to regard this as an erosion or drainage channel, and if it is, its true slope or gradient may after all be to the south into the main valley.

The borings for the Charlestown Bridge, connecting still more closely with the stoss slope of Copp's Hill, all ended on or in bowlder clay, proving the elevation of its upper surface to range between + 13.8 feet in City Square, Charlestown, and — 53 feet under the main channel, about 500 feet from Causeway Street in Boston. The three separate lines of borings agree very closely, each revealing a simple bowlder clay valley, with a short, steep slope toward Boston, rising to the surface in Causeway Street, and a long, gentle but undulating slope toward Charlestown; and the comparison shows quite plainly that the axis of the valley descends eastward, or toward the harbor. This valley is evidently not deep enough to be regarded as a down-stream continuation of the valley noted in the profiles south of the Warren Bridge; and we cannot escape the conclusion that the Warren Bridge marks the true divide for the bowlder clay as well as for the bed rock. The probability that the southern bowlder clay channel or valley descends either to the south or to the east becomes a practical certainty; although it is perhaps most probable that it descends both ways from a divide in the vicinity of Craigie Bridge, which would again bring the contours of the bowlder clay into harmony with those of the bed rock.

The Navy Yard borings all penetrate the bowlder clay, and the elevations of the surface of this deposit show again a fair degree of uniformity, although the extremes are + 7 and — 63, — a range of 70 feet. Four-fifths of the determinations fall between — 10 and — 40 feet, and over half of them between — 15 and — 35 feet. The contours of the bowlder clay show no regard whatever for the bed-rock valley previously noted as sloping to the northeast; and over the deepest part of this valley the bowlder clay attains an extreme thickness of 85 (— 13 to — 98) feet. The bowlder clay contours run lowest to the south, evidently declining toward a bowlder clay valley between the Navy Yard and the Man-of-War Shoals

drumlin, which may fairly be regarded as the down-stream continuation of the valley in the bowlder clay disclosed by the Charlestown Bridge borings; and it may be added that the depths are entirely favorable to that view. The farther extension of this valley, assuming it to be the product of stream erosion and a true drainage channel, may be either to the north, toward the deep, preglacial valley of the Malden River, or to the east, between Copp's Hill and the East Boston drumlins, the data in hand being insufficient for the determination of this point.

Under the harbor, on the lines of the East Boston tunnel borings, the surface of the bowlder clay has a fairly uniform elevation of —80 to —90 feet, averaging a little lower in the northern or North Ferry profiles than in the southern or South Ferry and State Street profiles. The flatness or approximately plane character of the surface of the bowlder clay is quite as marked here as under the Charles River, although the actual elevation is 20 to 50 feet less. That this great depth of the bowlder clay continues and increases around the south and west sides of Copp's Hill is shown by the failure of all the East Boston tunnel borings in the State Street section to get below the blue clay, and the fact that the artesian wells on North Street found the blue clay resting directly on the slate bed rock at a depth of 104 feet.

At many points the bowlder clay is separated by a few feet of bluish (unoxidized) sand and gravel, often more or less clayey, from the blue clay, giving a gradation from the bowlder clay into the blue clay, and showing that the former was exposed somewhat to the sorting action of water at the beginning of the deposition of the latter. A feature of the bowlder clay of still more special interest is found in the interstratified beds of washed material, including gravel, sand and clay. This has been noted in some of the borings for the Charlestown Bridge; and in at least ten of the Navy Yard borings the bowlder clay is divided by one and in some cases two layers of sand, varying from 1 to 5 feet in thickness, and separated by 15 to 20 feet of bowlder clay. This intercalation of limited layers of washed material in the bowlder clay is not uncommon; but it is usually confined, as in this instance, to the lee slopes of drumlins, the Navy Yard borings being directly in the lee of the Bunker Hill drumlin; and this relation is very satisfactorily confirmed by the East Boston tunnel borings in the lee of Copp's Hill and the

subway borings in the lee of Beacon Hill. This principle would exclude washed material from the bowlder clay north of Beacon Hill; and this is precisely what, with unimportant exceptions, the several bridge profiles show. The exceptions are impervious blue clay, and no facts have come to light indicating that the bowlder clay in the vicinity of the site of the proposed dam falls below the normal as regards either firmness or impermeability.

Glacial Lake Shawmut.

During the final disappearance of the ice sheet, the ice lingered longer, as previously stated, in the valleys than on the uplands, and much longer in the basin of Boston Harbor and Massachusetts Bay than over the country to the westward, including the main part of the Boston basin. The eastward drainage was thus impounded, forming the glacial lake to which I have given the name of Shawmut, communicating on the southeast with glacial Lake Bouvé during the time when the latter discharged eastward into Cohasset Harbor. At its highest stage the surface of Lake Shawmut was about 70 feet above the present level of the sea, the elevation being marked by extensive delta plains of sand and gravel formed by the tributary glacial streams, the courses of which are now marked, in some cases, by winding ridges of gravel known as eskers. With the continued recession of the ice, successively lower outlets for the united waters of lakes Shawmut and Bouvé were opened, and we find, in consequence, eastward from the 70-foot plains, extensive delta plains at elevations of 40 and 20 feet, approximately, and extending in the south part of the Boston basin to the present shore of the harbor.

While these deposits of relatively coarse detritus, resulting from the washing of the bowlder clay or ground moraine as it was being set free by the melting of the ice, were forming in the shallow marginal portions of Lake Shawmut, adjacent to the northward-receding margin of the ice, the finer material (quartz flour and clay), once incorporated with the coarse in the composition of the bowlder clay, was being deposited in the deeper and more tranquil part of the lake, remote from the mouths of the glacial rivers. Thus was formed the important deposit known as the blue clay or glacial clay. It was laid down in regular horizontal layers, and probably completely filled the basin of Lake Shawmut up to the highest level now reached by the clay, which is about 5 to 10 feet above the present high-tide level.

The Blue Clay.

Under Boston Harbor and its tributary estuaries we find above the bowlder clay, or above the bed rock where the bowlder clay is wanting, in normal order the blue clay. This, as we have seen, is a true glacial clay, a deposit of impalpable detritus from the waters of the glacial lake (Lake Shawmut) which came into existence as the ice retreated from the area of Boston Harbor, the land being still much more elevated than at present. This body of fresh water, free from tidal currents, and frozen over during a large part of each year, presented, in its freshness and tranquillity, conditions exceptionally favorable for the deposition of quartz flour and clay. That the blue clay is not marine is proved by the entire absence of fossils, and the fact that similar clay is not being deposited in the harbor at the present time, except perhaps to a limited extent on the eel-grass flats. It is in the main a very tough, plastic clay, but containing, as do all glacial clays, a large portion of impalpably fine sand or quartz flour. There are, however, occasional thin streaks and layers of true sand, representing periods when there was more motion in the water.

The angular fragments and grains of rock, of all sizes up to bowlders several feet in diameter, scattered irregularly here and there through the clay, as so well shown by the East Boston tunnel, and most abundantly, as a rule, toward the bottom of the deposit, are a very characteristic and significant feature of the clay. This material could not have been borne in suspension by the same currents that deposited the clay, but it was undoubtedly dropped by floating ice — floe ice and icebergs. Another convincing proof of the glacial origin of the blue clay is found in the fact that in a number of the East Boston tunnel borings, on the west side of the harbor, and more or less in the lee of the Copp's Hill drumlin, the clay is divided, usually near the bottom, by a sheet of bowlder clay from 10 to 25 feet in thickness. Similar phenomena have been observed elsewhere, as in the lee of the Beacon Hill drumlin, and, as previously noted, in one of the Charlestown Bridge borings. Apparently, this means that when the deposition of the clay began in this part of the harbor the margin of the ice sheet was still near by, so that a slight readvance of the ice spread a layer of bowlder clay over a part of the blue clay; and when the ice again retreated, this intrusive sheet of bowlder clay was in its turn covered by a considerable thickness of the blue clay.

A more probable explanation, however, is found in the agency of floating ice, as for the disseminated glacial detritus.

The borings show that the clay beds reach an extreme elevation of about 5 feet above high tide, which accords well with observations made in the clay pits of Everett and West Cambridge; and it extends to a depth of 80 to 90 feet below low tide in many of the East Boston tunnel borings, and to still greater depths, down to nearly 200 feet below the same datum in artesian wells and borings located in the deeper bed-rock valleys. The under surface or bottom of the blue clay is in general, of course, the upper surface or top of the bowlder clay, except for the bed of sand or gravel, of no great thickness, which occasionally intervenes; and it is improbable that the maximum depth of this contact has yet been determined. There can be no doubt, however, that, since the clay must have been deposited in perfectly horizontal, even layers, and have covered the entire area to about the level of the highest point which it now attains, its maximum original thickness in the inner part of the harbor was not less than 200 feet.

On the draining of Lake Shawmut by the farther recession of the ice, the clay deposit, which was then still at a considerable elevation above the sea, was exposed to the air long enough (hundreds and probably thousands of years) to permit the Charles and other streams to erode valleys in it to maximum depths of 50 feet or more; and, since in this harbor area the preglacial channels of the rivers had been completely effaced by the deposition of the blue clay, the new channels are more or less independent of the old. This we have seen is markedly true of the lower or tide-water portion of the Charles. It was at this time, as the result of some relatively slight and wholly fortuitous inequality in the surface of the clay deposit or of the sand, a slight thickness of which was here and there spread over the surface of the clay in the closing stages of Lake Shawmut, that the Charles first began to follow its present course below the Harvard Bridge. That the erosion of the clay, producing all the depressions now occupied by the inner harbor, was subaërial and not marine — fluvial and not tidal — and that it extended over a long time, are indicated by the superficial yellowing of the clay through the oxidizing influence of the atmosphere; the oxidation extending commonly to depths of 0 to 10 feet below the present upper surface of the clay, even under the bed of the river.

This is an important point, since it proves conclusively that the estuary of the Charles is not due to tidal scour, but is the product of the river at a time when the land stood higher relatively to the sea than now.

During the subsequent slow subsidence of the land the erosion of the bed of the river ceased, and, instead of being further degraded, it was somewhat aggraded by the deposition of sand and fine gravel to varying depths; the borings for the Charles River bridges showing, resting unconformably upon the eroded surface of the blue clay, from 0 to 20 feet of sand and gravel, the prevailing thickness being from 5 to 10 feet. This deposit, which appears to become thicker landward and thinner and less continuous seaward, is probably in part marine — a beach formation, just as we may now find at various points about the harbor beaches of sand and gravel forming over the blue clay as well as the bowlder clay. In part, also, it may be regarded as residuary, an accumulation of the stones once incorporated with the blue clay which has been removed by fluvial erosion.

The harbor as we now know it came into existence with the subsidence of the land to approximately its present level, and the inner harbor, at least, is confined almost wholly to the valleys which had previously been formed by fluvial erosion in the blue clay. With farther subsidence, carrying these deposits below the sea level, the sand and gravel gradually gave way to the silt, or the black, carbonaceous, sandy mud or muddy sand, which everywhere forms the immediate floor of the harbor below the Boston base.

Since the blue clay is the principal deposit above the bowlder clay, it demands special consideration. Careful mechanical analyses of the blue glacial clay of this region show that it invariably contains a large proportion of quartz flour, which detracts but slightly from its clayey qualities, while adding to its value for brickmaking, etc., by tempering the clay. At its higher levels, and almost everywhere above the low-tide level, the clay has been, as previously noted, superficially oxidized to a buff or yellow color. The fact that the yellow or oxidized clay, and also the oxidized bowlder clay, is found from 10 to 20 and even 30 feet or more below low tide, indicates that the glacial lake was drained and the deposit exposed to the air for a long time before the land subsided to its present level relatively to the sea.

Both the oxidized and unoxidized clay are naturally of a very

stiff, tough, and impervious character; and this, together with the considerable weight which they bear, must keep them comparatively dry, or free from any excess of water. The oxidation makes the clay, and also the bowlder clay, harder and firmer, by cementing the clay particles with iron oxide; and this may explain the fact that the boring records often indicate "hard clay" above, passing downward through "stiff clay" to "soft clay." As regards its imperviousness, it must be noted that the formation as a whole in its natural position must be more impervious to the overlying water of the harbor than filtration experiments with a representative series of samples would indicate; because the stratification of the clay must be strictly horizontal, and the highly impervious or non-pervious layers of plastic clay prevent the water from gaining access to the occasional relatively pervious sandy layers.

One of the most interesting sections, as regards the light which it throws upon the relations of the blue clay, is that based upon the borings made preparatory to dredging on the southwest side of the Bird Island flats. This shows, toward the west end of the flats, and from the bottom upwards: first, bowlder clay, forming a well-defined valley, which is filled with, second, blue clay, the blue clay being soft below and passing upward through stiff to hard, the hard clay being rather thin, and in part yellow instead of blue, as the result of oxidation.

The Silt.

"Silt" is used here as a general name for the recent deposits (including those now forming), which are of a fine or muddy character. The blue clay is covered normally by 2 to 5 feet or more of soft, black (carbonaceous), sandy mud, or, more properly, a fine, muddy sand, which commonly contains shells or fragments of shells, and is thus strongly contrasted with the blue clay. Wherever streams had excavated hollows in the surface of the blue clay, these are partially or wholly filled with silt, which there attains an exceptional thickness — 15 to 20 feet in some cases. Other instances where this sandy silt has an exceptional thickness are best explained as due to the dredging of the silt and its use for filling. In some instances, also, the silt is less carbonaceous, and passes into a fine sand.

The silt is an entirely loose and uncompacted deposit, which is easily moved or drifted about, like sand on a beach, by the action of

the current; and hence areas from which it must once have been removed by dredging, as about the wharves, are now in general covered by it again, so that it is, in fact, a nearly universal deposit in this part of the harbor. That the silt is very sensitive to variations in the force of the currents is shown by the fact that in a more sheltered area, like the angle between the Charles and Mystic rivers, off the Navy Yard, it attains a much greater thickness — commonly 10 to 15 feet, with a maximum of 25 feet. The fact that the deposition of this relatively coarse material between Boston and East Boston is almost at a standstill now is proof sufficient that the deposition of the blue clay belongs entirely to the past, and to a somewhat remote past; for we have incontestable evidence that the deposition of this sandy silt began a long time ago and has witnessed a notable change in the relative levels of the land and sea. Innumerable borings and excavations in the low lands all about Boston and in the valleys of the Charles and Neponset rivers, etc., have shown that this highly fossiliferous silt, containing many shells no longer living in Boston Harbor, rests upon the blue clay and is covered by a considerable thickness of peat. The peat is largely now below sea level, and thus proves that a subsidence of the land has taken place. This postglacial subsidence, tending to deepen the harbor, has made the conditions increasingly favorable to the deposition of the silt.

The slow subsidence of the land which made the accumulation of the silt possible has continued during the whole period of its accumulation; and we have good reason to believe that this subsidence is still in progress, and that the silt is still accumulating. The average or normal rate of increase of a deposit of this character must, in the nature of the case, be extremely slow; and that it has been slow in this instance, and that it began a long time ago, is proved by the fact that it has not only witnessed a notable change in the relative levels of the land and sea, but also a notable climatic change, for it contains species of shells no longer living in Boston Harbor or north of Cape Cod. It is probably entirely within bounds to say that the deposition of the silt has covered a period of fully five thousand years, the rate varying according to the locality, from less than 1 foot to 5 feet in a thousand years.

It is easy to see that for any given locality the rate must diminish as the subsidence progresses and the depth of the water increases. Hence, except for the wastes from sewers and the greater

wash from streets and ploughed ground than from the natural forest covered drainage area, we may fairly assume that the rate of deposition at the present time for the estuary of the Charles is less than the average for the past. A rate above the normal is possible only in a relatively sheltered area, or where, through some change in the strength or direction of a current, silt that has been deposited is swept away, to be redeposited in a more quiet place. In other words, original deposition must be slow, and slower now than formerly, unless increased by artificial causes; and redeposition only may vary widely from the normal rate.

The silt, as now distributed, is in part distinctly or highly fossiliferous, and in part free or comparatively free from shells. Not infrequently the same boring shows it to be free from shells above, and shell-bearing below. Obviously, the most if not all of the shells are too heavy to be transported by the tidal currents, and hence where the silt is suffering erosion the shells are left behind, gradually forming a residuary accumulation or layer, which must tend to protect the silt from farther erosion, and the material which has been swept away is deposited in some more tranquil spot, free from shells. Hence the absence of shells may be regarded as an indication of transportation from the point where the material was originally deposited; and it is a safe conclusion that the erosion would have been much more extensive than it has been, but for the shells.

We have noted that the average rate of deposition of the silt must have been greatly reduced by the construction of sea walls, wharves, etc., in the harbor, and of dams on the river, and that the proposed dam would operate very efficiently to the same end by permanently cutting off a vast amount of material which might conceivably be swept out into the harbor, and, by diminishing the volume of the tidal reservoir, and consequently the movement of the tidal prism, lessening the power of the tidal currents to transport detritus remaining below the dam and exposed to their action. This principle appears still more important when we reflect that the chief source of detritus in the past has been, not the river, but the shores, islands and flats of the harbor. In other words, the prevailing movement has quite certainly been inward and not outward, the estuaries and bays being slowly but surely filled up and obliterated by contributions chiefly from the sea and not from the land. This conclusion is greatly strengthened by the obvious fact that the in-

coming tide must be the more efficient agent of detrital transportation, since, as has been confirmed by recent observation, the cold salt water of the flood must be heavier than, and consequently will have some tendency to flow beneath, the relatively warmer fresh water of the ebb tide.

A most striking illustration of the inefficiency of fluvial transportation in this region is afforded by the fact that the Mystic Ponds, occupying kettle holes, or depressions in the modified drift due to the melting of residuary and buried masses of ice, and therefore dating from the close of the ice age, have not been obliterated or even appreciably diminished in area by the action of the river during a period estimated at ten thousand years. In this connection we may also pertinently note that the shells in the silt not only protect it from erosion, but, like pebbles on a beach, favor its accumulation by affording in the dead water of interstitial spaces an opportunity for sand and silt to settle. The last thought suggests another. Apparently the shells in the silt are all dead, some of them, at least, having become so since the settlement of this region by Europeans, and probably as an incident, or indirect consequence, of the increasing density of the human population; and it may be doubted if, in the absence of its organic accompaniment, the accumulation of silt could continue at its normal rate on tide-swept areas. On the other hand, Dr. Field has pointed out that the extinction of some if not all of the molluscan types, and notably of the long oysters, was due to an excess of silt, the abnormal length of the oysters being interpreted as due to an unconscious effort on the part of the organism to keep pace with the growth of the sediment which finally overwhelmed it. This crisis might perhaps reasonably be explained as a consequence of the deforesting and cultivation of the land, making it more easily eroded. But the tendency is clearly in the opposite direction now, for shore defences, paved streets, intercepting sewers, the covering of extensive areas by buildings and the general restriction of cultivation to turf and trees must have greatly checked both marine and subaërial erosion, and, in consequence, the complementary process of deposition must be nearly at a standstill, so far as it depends upon land-derived detritus; and we have in future chiefly to guard against the inward transfer by the deep running flood tides of the immense deposit of silt in the outer harbor. Certainly one important means to this end is the reduction of the tidal reservoirs.

While the early development of civilization in this district probably tended, for the reasons stated, to accelerate the deposition of the silt and to extinguish the organisms characteristic of the older and deeper portions of the deposit, the later developments have undoubtedly operated to retard the deposition of the silt, even reducing it below its normal or pre-colonial rate; and we may anticipate that the tendency to shoaling will be diminished by the deepening and broadening of the channel by dredging now or recently in progress.

Conclusion.

That the waterways of the inner harbor are not due in any appreciable degree to the erosive action of the tides, and that wave erosion tends only to the obliteration of the channels, are propositions which should require no further argument. Postglacial deposition aside, the subaqueous contours are the product either of the glacial agencies in the laying down of the drift formation, or of the subaërial or stream erosion of the glacial deposits, and especially of the blue clay. That the erosion was subaërial is proved by a variety of features, — especially by its occurrence, in general, only where required by the existing drainage systems of the land; and by the superficial oxidation of both the bowlder clay and the blue clay, even where covered by a considerable depth of highly carbonaceous silt. The land valleys thus developed below the present level of the sea were drowned by the subsequent subsidence which made possible the deposition of the silt in them. That the rate of subsidence has, in the main, exceeded the rate of deposition of the silt, the channels deepening in spite of the deposition, is obvious, for otherwise the channels must have been filled and obliterated; and that the subsidence is probably still in progress is indicated by many facts noted on this and other parts of our coast, such as the submerged forests and peat beds, and the wearing away by the waves of aboriginal shell heaps and graves. But that the rate of subsidence has probably diminished would seem a safe inference, in view of the extensive development over the inter-channel areas of eel-grass flats, subsequently, in large part, converted into salt marsh, on which peat has formed more or less extensively. In fact, the breadth of fully developed marsh in some parts of the harbor, and the approximately uniform elevation of even our broadest beaches, such as Nantasket,

are suggestive of a good degree of stability at the present time;[1] and that the subsidence has been more or less intermittent is indicated by peat beds interstratified with the silt, and now 10 to 20 feet below the minimum elevation (high tide) at which peat can form. That the movement has not actually been reversed, or at least that the downward movement has dominated throughout postglacial time, is indicated by the facts stated, and also by the absence of the carbonaceous silt, with or without its characteristic fossils, above sea level.

That the silt deposition has in the past lagged far behind the subsidence is obvious, the average thickness of the silt being but a small fraction of the average depth of the harbor to the bottom of the silt. We are thus brought once more to the conclusion that only redeposition of the silt, or its transfer from one point to another, like drifting snow, can lead to appreciable shoaling of the harbor.

The argument that if the tidal scour were diminished, as it would be by any reduction of the tidal reservoir, Boston Harbor would fill up and become shallow, like Quincy and Dorchester bays, where there is very little tidal scour, is based on the assumption that these bays were once deep, and have silted up. But this assumption is wholly unwarranted. In the case of Quincy Bay, between the Neponset River and Weymouth Fore River, there is no tributary stream of sufficient magnitude to have excavated, during the time when the coast was more elevated, channels comparable in depth and breadth with the lower estuary of the Charles. The known facts indicate, rather, that the low sand plain of North Quincy extends eastward under this part of the harbor, affording a foundation for the broad areas of eel grass, in the meshes of which some mud has been slowly entrapped; but that the mud or silt has attained important thickness is improbable.

In Dorchester Bay it appears, from the borings made in connection with the construction of the main drainage tunnel, that in ancient times, prior to the general subsidence of the district, the Neponset River excavated a channel in the blue clay to a depth of

[1] As previously referred to, the State geologist of New Jersey has deduced from varied and manifold data a probable rate of subsidence of the coast in the vicinity of New York Harbor at the present time of about 2 feet per century; and yet the beach and marsh developments of that coast are fully equal to those of Boston Harbor.

between 50 and 60 feet below the present low-tide level, and that in this channel the silt now has a maximum thickness of about 25 feet. It should be noted, however, that, encircled as it is by land largely composed of modified drift in the form of fine sand, the conditions have here been exceptionally favorable to the comparatively rapid accumulation of the silt. It is easy to see that, during the slow submergence of such low, sandy tracts as we have in North Quincy and the eastern part of Dorchester, the sand would be worked over extensively and deeply by the waves, and much carbonaceous mud incorporated with it, and the sandy silt thus developed at a much more rapid rate than would be possible after submergence became an accomplished fact.

The bowlder clay which elsewhere constitutes so large a part of the shores of the harbor, particularly around the upper harbor, and the lower part of the estuaries of the Charles and Mystic, erodes much more slowly, and, when worked over, as during the slow subsidence, yields to the waves chiefly stones and gravel which remain on the beach, and quartz flour and clay which cannot settle in the tidal channels, but are likely, so far as not entrapped in the meshes of the eel grass, to be swept out to sea by the ebb, and deposited in deep, quiet water off shore. This enables us to understand how it is that the channels of the inner harbor have survived submergence, and that in some cases they are almost bare of silt. It is especially interesting to note that on the shores of the inner harbor, in Boston, Charlestown, East Boston and South Boston, easily eroded, sandy drift is conspicuous by its absence, and the floor of this part of the harbor is but lightly covered by silt; but above the Charlestown bridges, in Cambridgeport and Brookline, the shores are largely fine sand, and the upper portion of the estuary of the Charles is deeply silted above the surface of the blue clay.

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.

By ARTHUR A. NOYES.

(Preliminary Publication.)

INTRODUCTION.

The aim of this investigation has been to work out in detail a systematic, universally applicable scheme of qualitative analysis which shall include as nearly as practicable all the metallic elements, and which shall make possible their detection even when present in quantity as small as one or two milligrams.

The great importance, both from a technological and a purely scientific standpoint, which has become attached in recent years to many of the "rare elements" — so called often only by reason of their traditional and somewhat arbitrary exclusion from the usual schemes of qualitative analysis — has made it highly desirable that a systematic and reliable method for their detection be available. Any chemist who, without previous experience in this field, has occasion to test for small quantities of these elements will infer upon consulting the existing literature, and become convinced when he begins to experiment, that his problem is beset with difficulties and will require much time for its solution.

Until within a few years, aside from the brief outlines given in the text-books on Qualitative Analysis of Rose, Fresenius, Classen, and a few other writers, nothing like a systematic scheme of analysis existed; and it was necessary for the analyst to apply as best he could the isolated separations and tests recorded in such text-books and in the journals. In 1898 Carnot published in his "Traité d'analyse des substances minérales" a scheme of qualitative analysis which included all the more important rare metals. But none of these methods seem to have been subjected to any adequate investigation with reference to the effectiveness of the separations or the reliability and delicacy of the tests; moreover, in a field of work where

the closest adherence to the proper conditions is essential to success, the directions given are of a most general character. These schemes, therefore, when tested in the laboratory, are found to be seriously defective, and to have little practical value, except for the detection of large quantities of some of the rare elements. A vast amount of valuable work has, of course, been published upon the separation of the rare elements of separate groups, like the rare-earths, the platinum-metals, and the rarer alkali-metals; but this work has been done mainly from the standpoint of quantitative analysis and with reference to the limited number of elements which are found associated in certain important minerals or ores. Of the systematic procedures devised for qualitative purposes ought to be mentioned, however, those of Mylius and Dietz (*Ber.*, **31**, 3191. 1898) and of Leidié and Quennessen (*Bull. soc. chim.* (3) **27**, 181. 1902) on the platinum metals, and of Possetto (*Chem. Centralb.* 1898, **1**, 634) on the rare-earths. These quantitative and qualitative investigations have furnished many of the data necessary for the working out of a complete system of qualitative analysis, such as that which forms the object of this investigation.

This work has been in progress for over three years, and has been carried on in large part by research assistants and advanced students, whose valuable aid will be given recognition in connection with the separate groups of metals upon which each worked. The investigation has been liberally assisted by grants from the Warren Fund of the American Academy of Arts and Sciences, and will be published in its final form in the Proceedings of that Academy. It has been thought advisable, however, to make in this journal a preliminary publication of the work, as fast as integral portions of it are brought into satisfactory shape, so that the method may be available at once to those who may desire to use it. The work upon it will be continued, in order to test it more thoroughly and to improve it in matters of detail; but it is not likely that the procedure will be radically modified.

The results will be presented in the form that seems best adapted to the purposes of the analyst. The System of Analysis will be primarily divided into a series of Parts, in each of which will be described, as a rule, the detection of the elements precipitated or otherwise separated by a group reagent. Part I will treat of the Preparation of the Solution; Part II, of the Analysis of the Tung-

sten and Niobium Groups; Part III, of the Analysis of the Selenium and Silver Groups; Part IV, of the Analysis of the Platinum Group and the Detection of Lead and Tellurium; Part V, of the Analysis of the Ruthenium, Iridium, Copper, and Molybdenum Groups; and the succeeding Parts, of the Rare-Earth, Aluminum and Iron, Alkaline-Earth, and Alkali Groups. Under each Part is first presented a Tabular Outline which will give a survey of the important steps and the chemical reactions involved in the procedure. This is followed by a General Discussion, in which are presented the reasons for the adoption of the process employed. Then comes the Procedure itself, and the explanatory Notes upon it. Next are presented Confirmatory Experiments and References, which serve to substantiate the statements made in the Notes and to justify the details of the Procedure. Finally are given the Test Analyses, which were made with known mixtures according to the procedure, in order to test its efficiency.

The reader who wishes only to get a general idea of the method and its efficiency will find that the chapters entitled "Tabular Outline," "General Discussion," and "Test Analyses," will suffice for his purpose. The actual analyst will utilize especially those entitled "Tabular Outline" and "Procedure and Notes." Only to investigators in similar lines, or to those who seek the justification of the statements made in the Notes will the chapters on "Confirmatory Experiments and References" be of interest.

The operations are described in the Procedures in much detail; and the reasons for them, the theoretical principles involved, and other incidental matters are presented very fully in the Notes. It may well seem to experienced analysts that the writer has gone to an extreme in this respect: but, in the first place, attention to not obvious details is really essential in many cases in order to secure delicacy of the tests; and, secondly, it has seemed best to make the scheme as effective as possible in the hands of chemists with little experience in this kind of work, even though it involves in some cases rather lengthy descriptions. Even with such a full description, a knowledge of the manipulation of exact qualitative analysis is essential, in order to enable one to detect small quantities of some of the elements. Before analyzing an unknown substance, any one using the method for the first time should apply the procedure of each group to a known mixture containing two or three milligrams of each element.

The directions are almost always given in the form applicable to the case where all elements that could be present are present, the modifications admissible when certain operations lead to negative results being usually sufficiently evident. The scheme is divided into a number of separate "Procedures," a new one being begun whenever the substance has been resolved into two parts (such as a precipitate and filtrate) which are to be submitted to different operations, or whenever two or more collateral procedures converge to a single one. In order to make it possible to see at once the proper sequence of the procedures in an actual analysis, they are numbered consecutively in the description (except that some numbers are omitted at the end of each Part to facilitate subsequent revision); and at the beginning of each procedure the one by which the substance was last treated, and at the end of each procedure those by which the two separated portions of it are next to be treated, are referred to by number.

Most of the experiments described under "Confirmatory Experiments and References" are undoubtedly merely confirmations of previously known chemical facts. The application of these facts to the specific conditions of the procedures it was, however, constantly necessary to test; and it has seemed worth while to make the results a matter of record. The experiments are preceded by a reference to the procedure and note to which they relate.

Of the abbreviations employed, only a few need be explained: G. D. is used for General Discussion; P., for Procedure; N., for Note; C. E., for Confirmatory Experiments; T. A., for Test Analyses. A number within parentheses expresses the specific gravity at 15°: even with diluted acids, the concentration is for brevity usually indicated in this way; thus HCl (1.02) means an acid made by mixing one volume of HCl (1.12) with five volumes of water. When it is directed to add a variable quantity of a reagent (for example, 5–15 ccm.), the amount used should be adjusted to the size of the precipitate or residue. Certain brief expressions commonly employed in the procedures are fully explained, especially with reference to the manipulative details, under one of the first procedures where they occur; for example, see P. 3, N. 2, as to the exact significance of "evaporate just to dryness," P. 5, N. 6, as to that of "wash the precipitate."

TABULAR OUTLINE.

Non-metallic substance: *Heat 1 gm. with HNO_3 (1.20), dilute and filter.* (*P. 1.*)

Residue: *Heat with HF, evaporate with HNO_3, and add HNO_3 (1.05); (if insoluble fluorides remain, digest with SiO_2;) evaporate, and heat at 120°.* (*P. 3.*)

Solution: *evaporate, and heat at 120°.* (*P. 2.*)

Metallic substance: *Heat 0.5 gm. with HNO_3 (1.20), evaporate, and heat at 120°.* (*P. 4.*)

Dehydrated residue: *Heat with HNO_3 (1.20), dilute, and filter.* (*P. 5.*)

Solution: all elements except Si, Nb, Ta, W, Sn, Os, and most of the Sb and Ti. (*P. 51.*)

Residue: *Heat with HF, dilute, and filter.* (*P. 6.*)

Solution: niobium and tungsten groups, (Nb, Ta, Ti, W, Sn, Sb); sometimes also P, As, Bi, Se, Te, V, Mo, Ge. (*P. 31.*)

Residue: MnO_2, PbO_2, HgS, Au, and the substances named below under "residues." *Boil with HCl (1.20), then with aqua regia, dilute, and filter.* (*P. 7.*)

Solution: *evaporate, add HCl (1.02), filter.* (*P. 17.*)

Solution: chlorides of Pb, Mn, Hg, Au, Pt. (*P. 71.*)

Residue: AgCl, $PbCl_2$, $PbSO_4$, $BaSO_4$, $SrSO_4$. (*P. 18.*)

Light-colored non-metallic residue: $BaSO_4$, some silicates, Al_2O_3, TiO_2, $ZrSiO_4$, SnO_2, ThF_4, monazite. *Fuse with Na_2CO_3; heat with water, and filter.* (*P. 9.*)

Solution: (*P. 11.*)

Residue: *add HCl and filter.* (*P. 10.*)

Solution: (*P. 71.*)

Residue: *Fuse with $K_2S_2O_7$.* (*P. 12.*)

Dark-colored or metallic residue: C, SiC, MoS_2, $FeCr_2O_4$, $Fe_7(CN)_{18}$, Pt, Ir, Os, Rh, Ru, $FeSi_x$, $FeCr_x$, etc. *Fuse with Na_2O_2, add water and HCl, and distil into NaOH.* (*P. 13.*)

Distillate: OsO_4. (*P. 14.*)

Residual solution: (*P. 15.*)

General Discussion.

Much effort has been devoted to determining the best general method for the preparation of a solution of an unknown substance for the analysis for the metallic elements. That some definite method be adopted for this purpose is an essential preliminary to the working out of a general system of analysis, especially when the rare metals are to be included; for the subsequent division into groups must depend to some extent upon the nature of the acids employed as solvents. The aim has been to devise a method of preparing the solution, which in its actual application to substances ordinarily met with shall be as rapid as possible, which shall be so general and so fully developed as to effect the solution of practically all known substances, and which shall adapt itself to sharp and convenient group-separations in the subsequent system of analysis.

In the usual, well-known method of procedure with a non-metallic substance this is heated successively with water, dilute and concentrated hydrochloric acid, nitric acid, and aqua regia. Then the residue, if blowpipe tests show the absence of much reducible metal, is fused in a platinum crucible with sodium carbonate; or, if reducible metal is present, to remove it the residue is first treated with special solvents like potassium cyanide and ammonium acetate, and is then fused in a platinum crucible; or, if the use of such solvents is inconvenient or ineffective, the residue is fused in a porcelain crucible, whereby the constituents of the crucible are introduced. Finally, any residue undecomposed by the carbonate fusion is fused with such special fluxes, potassium disulphate, sodium carbonate and nitrate, sodium carbonate and sulphur, as the apparent nature of the residue suggests. It will be seen that this procedure is very different from the one summarized in the Tabular Outline given above, which has been adopted as a part of the new System of Analysis. The advantages of the proposed modifications should therefore be presented.

An important consideration having a direct bearing on the procedure to be adopted for the preparation of the solution must be

first mentioned. This has reference to the fact that certain oxides, namely, those of silicon, tungsten, niobium, and tantalum, do not dissolve, or at any rate do not remain in solution, in the dilute mineral acids commonly employed; so that, when a substance containing these oxides has been brought into solution by an alkaline fusion or treatment with a special acid like concentrated sulphuric or hydrofluoric acid, they separate upon neutralization of the alkali or upon dilution or replacement of the acid, either immediately or in some subsequent stage of the analysis. This fact has been ignored in the previous schemes of analysis outlined for the rare elements; thus tungsten, in spite of the insolubility of its oxide in acids, is provided for either in the ammonium sulphide solution of the hydrogen sulphide precipitate, or in the filtrate from the ammonium hydroxide and sulphide precipitate; niobium and tantalum, which are bound to precipitate through hydrolysis of their salts when the solution is diluted and heated in the precipitation with hydrogen sulphide, are commonly included among the elements precipitated by ammonium hydroxide. It is therefore essential, unless these elements are to be allowed to appear somewhat capriciously at different points in the analysis, to remove them at the start. In order to do this completely, however, it is necessary to evaporate the solution to complete dryness, in order to dehydrate their hydroxides and make them completely insoluble in dilute acid. Even though it is true that certain other elements divide themselves between such a residue and the solution, and must be provided for in the subsequent analysis of both portions, this is a far less serious objection than that justified by the failure to provide for the certain detection of tungsten, niobium, and tantalum. It is for this reason that the first series of operations after the decomposition of the substance with strong acids is directed to effecting the removal of the group of elements whose dehydrated hydroxides are insoluble in dilute acid.

The first solvent employed in the proposed method (P. 1) is nitric acid, not hydrochloric acid, the most cogent reason for this being that, if the latter acid were used, certain elements, namely, arsenic, selenium, germanium, mercury, and gallium, would be wholly or partly lost in the subsequent evaporations, owing to the volatility of their chlorides. Hydrochloric acid also has the disadvantage of causing the precipitation of silver, lead, mercurous, and thallous chlorides, and thereby making it impossible to determine whether com-

plete decomposition has been effected. Nitric acid, owing to its oxidizing power, is, moreover, a more general solvent; but it does on this very account have the disadvantage of oxidizing sulphides to sulphates and causing the separation of the insoluble sulphates of lead, barium, and strontium; and it is to reduce the amount of this oxidation and to make certain crystalline nitrates, like those of lead and barium, more soluble, that a somewhat diluted acid of the specific gravity 1.20 is recommended. Furthermore, nitric acid, unlike hydrochloric acid, leaves all the tin and almost all of the antimony in the insoluble portion of the dehydrated residue.

The first residue insoluble in nitric acid is not treated at once with aqua regia, because the latter solvent decomposes very few substances unacted upon by the former; because the disadvantages of hydrochloric acid just specified apply to its use in some degree; and because any residue undissolved by it, especially if not thoroughly washed, might retain chlorides which would cause the platinum vessel necessarily used in the next treatment with hydrofluoric acid to be attacked.

The residue undissolved by nitric acid is treated with hydrofluoric acid for the reason that this forms a simple method of dissolving silica and almost all silicates, which otherwise would have to be decomposed by a fusion with sodium carbonate or some other flux. The fusion with sodium carbonate has the disadvantages that the operation is less convenient; that it introduces alkali-metals into the solution, which must therefore be tested for in a separate solution prepared in some other way; and that, before the fusion can be carried out in a platinum crucible, the residue must be tested for reducible metals, and, if they are present, freed from them, as far as possible, by treatment with special solvents, like hot concentrated hydrochloric acid or ammonium acetate and potassium cyanide solutions. If, however, it is not desired to test for alkali-metals, and if reducible metals are probably absent, the residue insoluble in nitric acid (P. 1) may, if the sodium carbonate fusion is preferred to the treatment here described, be treated at once by P. 7 and then by the subsequent procedures.

Both the free and combined hydrofluoric acid must next be completely removed, in order to proceed satisfactorily with the analysis; for, otherwise, partial solution of the oxides of the tungsten and niobium groups would take place, and the glass vessels used in subse-

quent operations would be attacked. Its removal might be easily accomplished by a single evaporation with sulphuric acid to the point of strong fuming; and this would have the advantage of decomposing a few other substances (such as monazite and thorium fluoride) that are not much attacked by hydrofluoric and nitric acids. A great many experiments were made to test the applicability of this process of decomposition, so much used in quantitative work, to the purposes of qualitative analysis. It was abandoned, however, because the introduction of sulphuric acid complicates the subsequent procedure by preventing the complete separation of the hydroxides of certain elements of the tungsten and niobium groups when the acid is diluted, and by causing the precipitation of some basic sulphates as well as that of the insoluble neutral ones before it is certain that complete decomposition of the substance has been effected. Its abandonment was, moreover, made possible by the discovery of an alternative method of decomposing the insoluble fluorides. It was found, namely, that all of these, except thorium fluoride, are destroyed by concentrated nitric acid when its action is supplemented by the addition of finely divided silica. This substance evidently acts by combining with the hydrofluoric acid liberated by the strong nitric acid, thus enabling the reaction to become complete, in accordance with the Mass-Action Law; it was, in fact, this theoretical consideration that suggested its use.

With by far the larger proportion of substances apt to be submitted to analysis, any portion of the dehydrated residue that may be undissolved by dilute nitric acid (P. 5) consists only of silica and oxides of the tungsten and niobium groups, and dissolves completely when it is treated with hydrofluoric acid (P. 6). Still less frequently will there be a residue after the next treatment with hot strong hydrochloric acid and aqua regia (P. 7); for almost all of the fairly common substances previously unacted upon, such as manganese and lead peroxides, mercuric sulphide, silver chloride, lead, strontium, and barium sulphates, gold and platinum, are dissolved by these acids. The lengthy description of subsequent procedures, which is added in order to provide for nearly every possible case, must not, therefore, give the impression that the method here adopted is in its ordinary application long or complicated.

Of the subsequent fusions necessary in special cases, only that with sodium peroxide (P. 13) need receive any general discussion.

This flux, suggested by the work of Leidié and Quennessen (*Bull. soc. chim.* (3), **27**, 181. 1902) was adopted, because it undoubtedly furnishes the best solution of the difficult problem of bringing the rarer platinum metals into a soluble form. The process usually employed for this purpose consists of two parts: the metal is first brought into a fine state of division by fusing it with a large quantity of lead and treating the fused mass with nitric acid; the residue is then intimately mixed with sodium chloride, and heated to a dark red heat in a current of chlorine. Both parts of this process are extremely tedious and likely to yield incomplete results, even when only half a gram of metal is to be treated. On the other hand, when the metal is to be fused with sodium peroxide, mechanical processes readily reduce it to a sufficiently fine state of division, and the fusion need not be continued for more than twenty minutes. It is true that the nickel crucible, in which the fusion is best carried out, is much attacked by the flux; but the presence of nickel does not interfere at all with the detection of the platinum metals or of the other elements which are precipitated by hydrogen sulphide, nor does it interfere very seriously with the detection of the elements present in the precipitate produced by ammonium hydroxide or sulphide, since they can be separated from almost all of the nickel by treating the precipitate with dilute hydrochloric acid. It may be added that, before finally adopting this procedure, a few experiments were made on metallic iridium with the hope of effecting its solution by heating it to 200° in sealed tubes with bromine or with a mixture of bromine and concentrated hydrobromic acid; but the quantity dissolved was insignificant.

In concluding this chapter, it is a pleasure to add that I have been ably assisted in this part of the work by Messrs. J. E. Ober, G. V. Sammet, and W. H. Whitcomb.

Procedure and Notes.

Procedure 1. — If the substance is a metal, treat it by P. 4.

If the substance is not a metal, proceed as follows: Grind about 1.5 gm. in small portions in an agate mortar until it is so fine that no grit is perceptible when a little of it is rubbed between the fingers. Weigh out roughly about 1 gm. into a casserole, pour over it 10 ccm. HNO_3 (1.20), cover the dish, and digest the mix-

ture on a water-bath for 15 minutes, or as long as an action appears to be taking place. [If, however, it is thought necessary to test for the presence of osmium in the form of a salt, boil the substance in a distilling flask with HNO_3, and collect and test the distillate by P. 13 and P. 14.] Then add 20 ccm. boiling water, and allow the residue to settle. [If a light-colored spongy mass of sulphur has separated, remove it by means of a rod or spatula.] Decant the liquid through a filter. If HNO_3 seemed to be slowly attacking the residue, digest it with a fresh portion of HNO_3, dilute, and decant as before. Wash the residue with hot water twice by decantation, pouring the washings through the filter. Transfer the residue from the casserole and filter to a platinum dish by rinsing with a little water. Decant or evaporate off the water. (Solution, P. 2; residue, P. 3.)

Notes. — 1. In order to secure the decomposition of difficultly decomposable substances by the following procedures, it is of fundamental importance that the substance be reduced to a literally impalpable powder, a result that can often be obtained only by the long-continued grinding of the substance in small quantities at a time.

2. One gram of the substance is usually taken; for, since 1–2 mgm. of almost any element can be detected by this system of analysis, with one gram the presence of as little as 0.1–0.2% can be determined, which is ordinarily sufficient. It is treated with the acid in a porcelain vessel because of the possible presence of chlorides, which would attack the platinum vessel which has to be used in the subsequent HF treatment (P. 3). The HNO_3 solution is decanted and the residue is washed for this same reason, and also because in many cases the elements which form insoluble fluorides, of which calcium is the most common, are thereby removed, so that the subsequent treatment with SiO_2 (P. 3) becomes unnecessary. The treatment in a distilling flask when osmium can be present as a salt is to avoid the loss of this element by volatilization, as OsO_4. See P. 13, N. 9.

3. If HNO_3 attacks the substance with separation of a white precipitate, the latter may consist of hydrated SnO_2, Sb_2O_5, SiO_2, TiO_2, GeO_2, Nb_2O_5, Ta_2O_5, MoO_3, or of $BaSO_4$, $PbSO_4$, $SrSO_4$. Certain nitrates, especially $Pb(NO_3)_2$ and $Ba(NO_3)_2$, may also separate in crystalline form from the strong HNO_3; but these dissolve upon adding water and heating to boiling. If a dense yellow decomposition-product results, it probably consists of H_2WO_4. A spongy mass which becomes pasty on boiling the solution is sulphur.

4. If a portion of the substance is not attacked by HNO_3 (1.20), it probably consists of one or more of the following substances: the oxides and sulphates named in N. 3; the native or ignited oxides of aluminium, chromium, and zirconium; the peroxides of manganese and lead; the silicates and fluosilicates of many elements; sulphide of mercury; fluoride of calcium; the halides of silver; ferrocyanide of iron; carbon; silicon carbide.

Procedure 2. — Evaporate the HNO_3 solution (P. 1) as nearly to dryness as is possible without overheating the residue. Heat in a hot closet at 120° for one hour, or longer if the mass has not then become perfectly dry. (Residue, P. 5.)

Note. — 1. The evaporation to dryness and heating in the closet at 120° serve to dehydrate and make less soluble in HNO_3 silica and the hydroxides of the elements of the tungsten and niobium groups, which may at first be dissolved by the HNO_3. If the dry residue were strongly heated over a flame, mercury compounds might be volatilized, and iron, aluminium, and chromium oxides made insoluble.

Procedure 3. — Add to the residue insoluble in HNO_3 (P. 1) 5–10 ccm. pure concentrated (40%) HF solution, and digest on a water-bath for 15 minutes. Note whether complete solution takes place. Add 5 ccm. HNO_3 (1.42), and evaporate just to dryness. Cover the residue with HNO_3 (1.42), and again evaporate just to dryness. Add 10 ccm. HNO_3 (1.05), and heat to boiling.

If complete solution took place either on the addition of the HF, or if it occurs on the treatment with the HNO_3 (1.05), evaporate just to dryness a third time; then heat the dish for at least one hour in a hot closet at 120°.

If neither the HF nor the HNO_3 (1.05) produced a perfectly clear solution, evaporate the liquid just to dryness, loosen the particles from the dish, add 10 ccm. HNO_3 (1.42) and 1 gm. pure, ignited precipitated silica, cover the dish, and digest on a water-bath for three-quarters of an hour. Then evaporate the liquid just to dryness, and heat the dish for at least an hour in a hot closet at 120°. (Residue, P. 5.)

Notes. — 1. The HF used must leave no residue whatever after evaporation and gentle ignition, since otherwise foreign elements would be introduced. It must not contain H_2SO_4 in considerable amount,

since otherwise $BaSO_4$ and $PbSO_4$ may be left undissolved on the subsequent treatment of the dehydrated residue with HNO_3 (P. 5) and HF (P. 6), and since some of the hydroxides of the niobium and tungsten groups may dissolve. The presence of H_2SO_4 in it may be detected by adding to 3 ccm. of it 10 ccm. HCl (1.03) or 20 ccm. HCl (1.02) and 1 ccm. 10% $BaCl_2.2H_2O$ solution.

2. Whenever, as in the above procedure, it is directed to evaporate a solution "just to dryness," this should be done in such a manner as not to heat any portion of the dried residue much above 100°. This may be accomplished by heating upon a steam-bath, or more rapidly over a small flame, provided proper care be taken; in the latter case, after the solution has been reduced to a small volume, the dish must be kept constantly in motion so that the heated parts of the sides as well as the bottom are always wet with liquid, and when nearly dry the dish must be often removed from the flame and shaken in the air, so that the final evaporation will take place at as low a temperature as possible.

3. If the substance is decomposed by HF with the separation of a white precipitate, this indicates the presence of lead, bismuth, lithium, magnesium, or of an element of the alkaline-earth or rare-earth group. If no such precipitate separates, it shows the absence in quantity as large as one milligram in the part of the original substance insoluble in HNO_3, of lead, bismuth, calcium, and all the elements of the rare-earth group. Since LiF, MgF_2, SrF_2, and BaF_2 are somewhat soluble, these precipitates separate only in the presence of considerable quantities of the elements — in the presence of, roughly, 5 mgm. Li, 2 mgm. Mg, 8 mgm. Sr, 30 mgm. Na, when 5 ccm. HF are used.

4. The HF solution must not be evaporated to dryness without the addition of HNO_3; for much titanium and tantalum would then volatilize as TiF_4 and TaF_5. In the presence of HNO_3, however, the loss of these elements is inconsiderable, undoubtedly owing to the fact that this acid decomposes their fluorides. In the evaporation with HF and HNO_3 there is no loss of mercury, arsenic, selenium, germanium, or antimony — the elements which volatilize to some extent out of a boiling concentrated HCl solution.

5. If complete solution takes place on the addition of HF, the three evaporations with HNO_3 remove the HF completely, even in the presence of the elements titanium, niobium, tantalum, which have a great tendency to form complex fluorine-containing acids. In that case, the treatment with SiO_2 can be dispensed with; and this is desirable, whenever practicable, both because it saves time at this point and because it makes it possible to determine immediately upon the treatment of the dehydrated residue with HNO_3 whether or not elements of the tungsten and niobium groups are present.

6. In case the HF precipitate consists of even large quantities (500 mgm.) of PbF_2, BiF_3, LiF, MgF_2, SrF_2, or BaF_2, or of a small quantity (less than 50 mgm.) of CaF_2, the two evaporations decompose it completely, so that these elements pass into solution on adding dilute HNO_3, and the addition of SiO_2 is unnecessary.

7. If oxides of the tungsten and niobium groups are alone present in the first residue, these (with the possible exception of SnO_2) will yield a clear solution upon the treatment with HF (see P. 6, N. 1), but will again separate after the evaporations with HNO_3; in this case, in which HF, but not HNO_3, yields a clear solution, it is, of course, also unnecessary to treat with SiO_2.

8. When, however, CaF_2 or rare-earth fluorides separate in considerable quantity on the addition of HF, it is not practicable to decompose them by repeated evaporations with HNO_3 alone. But the addition of SiO_2 and digestion with it and strong HNO_3 effect complete decomposition of all the fluorides (except ThF_4, which may remain partially undecomposed as a dense crystalline powder). The SiO_2 combines with the HF that is liberated by the HNO_3, and thus, in accordance with the Mass-Action Law, enables the decomposition to become complete.

9. CaF_2, even when present in considerable quantity after the two evaporations with HNO_3, may yield a homogeneous, slightly milky colloidal solution upon the addition of dilute HNO_3. This must not be mistaken for a true solution, the production of which alone warrants the omission of the SiO_2 treatment.

10. The SiO_2 used must leave no residue whatever upon treatment with HF and evaporation of the solution. It may be prepared by diluting commercial water-glass with three times its volume of water, adding HCl as long as precipitation continues, decanting, boiling the precipitate two or three times with water, drying it in a hot closet, heating it two or three times with HCl (1.20), washing it till free from acid, drying it in a hot closet, and finally igniting it.

11. The heating at 120° is necessary in order to make silica and the oxides of tin, tungsten, and tantalum entirely insoluble in HNO_3. This is even more necessary after they have been dissolved by HF than when treated with HNO_3 alone. If the residue were overheated during the evaporations, other oxides, like those of iron, aluminium, and chromium, might not dissolve completely on the subsequent treatment with HNO_3.

Procedure 4.—If the original substance is a metal, convert it into a form that offers as much surface as possible by grinding it in an agate mortar, hammering it in a "diamond" steel mortar, filing it with a fine steel file, shaving it with a knife, or converting it

into borings with a drill. Weigh out roughly about 0.5 gm. into a casserole, pour over it, very gradually if a violent action occurs, 10 ccm. HNO_3 (1.20), cover the dish, and heat the mixture on the water-bath as long as any evolution of nitrous fumes occurs, adding more acid if the action is renewed thereby, or a little water if crystalline salts have separated. Then evaporate the liquid just to dryness, and heat the residue in a hot closet at 120° for an hour, or longer if the mass has not then become perfectly dry. (Residue, P. 5.)

Note. — 1. See P. 1, N. 3 in regard to precipitates that may separate during the HNO_3 treatment, and P. 3, N. 11 in regard to the dehydration of the residue.

Procedure 5. — Loosen the dehydrated residue (P. 2, 3, or 4) from the dish, and rub it to a fine powder with a pestle; add to it 5 ccm. HNO_3 (1.20), or 10 ccm. if it seems necessary, cover the dish, and heat on a steam-bath for 10 minutes. Note whether there is any residue whatever. If no residue can be seen, rub the sides of the dish with the rubber-covered end of a glass rod, and allow the liquid to stand 3 or 4 minutes. If there is a crystalline residue of nitrates, add enough water to dissolve it, and note whether an amorphous residue remains. Dilute with 20 ccm. water, and heat to boiling. If the substance was a non-metallic one, unite at this point the two portions (treated by P. 2 and P. 3), unless it is desired to know their constituents separately. Decant the solution through a washed filter, retaining in the dish as much of the residue as possible. If the residue is large in amount, heat it again with 5 ccm. HNO_3 (1.20), dilute with water, and decant the solution through the same filter. Wash the residue with HNO_3 (1.05), decanting the washings through the filter; and transfer it to a platinum dish. (Residue, P. 6; solution, P. 51.)

Notes. — 1. If SiO_2 has not been added, important conclusions can be drawn in regard to the absence of certain elements in the substance when nothing whatever remains undissolved upon treating the dehydrated residue with HNO_3 (1.20). The fact must not be overlooked, however, that in the dehydrated form even a very small residue or slight turbidity may correspond to an appreciable quantity of an element. A perfectly limpid solution and one that does not deposit any sediment whatever after a few minutes' standing must be obtained, if such conclusions are

to be drawn. Moreover, it should be noted whether such a solution results before diluting the HNO_3 (1.20) with water (or after diluting it with as little water as suffices to dissolve crystalline nitrates); for any residue is more difficult to recognize in a large volume of liquid.

In case no residue whatever remains, it shows the absence of silicon, tin, niobium, and tantalum in quantity as large as 1 mgm.; of antimony in quantity as large as 2 mgm., except when an organic hydroxy-acid is present; and of tungsten in quantity as large as 1 mgm., except when phosphoric or arsenic acid or an organic hydroxy-acid is present. It also indicates the probable absence of titanium in quantity as large as 1 mgm., except when zirconium is present.

Organic hydroxy-acids, like tartaric, lactic, and citric acids, dissolve Sb_2O_5 and H_2WO_4 with great readiness. H_2WO_4 also dissolves very readily when H_3PO_4 or H_3AsO_4 is present, owing to the formation of complex acids. The presence of arsenic, phosphoric, and organic acids is detected in the course of the subsequent procedure. Boric acid does not increase the solubility of any of the oxides of the tungsten and niobium groups. Moreover, it will not be present if the substance has been treated with HF; for even 1 gm. H_3BO_3 volatilizes completely upon evaporation with 5 ccm. of this acid and 5 ccm. HNO_3 (1.42). Even 500 mgm. of titanium may dissolve completely in the HNO_3 when much zirconium (500 mgm.) is present.

2. If SiO_2 has been added, the presence or absence of the tungsten and niobium groups cannot be determined until the residue insoluble in HNO_3 has been treated with HF, the solution evaporated with H_2SO_4, and NH_4OH and $(NH_4)_2S$ added (P. 6 and Part II).

3. The residue insoluble in HNO_3 may contain in addition to the oxides of the elements named in N. 1 the following substances: MoO_3, when molybdenum is present in quantities over 100 mgm., or when tungsten or tin is also present; GeO_2, when over 30 mgm. Ge are present; Bi_2O_3, when much antimony is also present; SeO_2 and TeO_2, when much tin or antimony is also present; ThF_4, when much thorium is present in the residue treated with HF; the phosphates and arsenates of tin, titanium, zirconium, and thorium, and the vanadate of tin, when the components of these substances are simultaneously present. The residue may also contain certain undecomposed substances (named in P. 6, N. 2) which are not attacked by either HNO_3 or HF.

4. Of the elements named in N. 3 which may under the specified conditions be present in the residue insoluble in HNO_3, the following ones always pass into the HNO_3 solution in considerable proportion when large quantities of them are present: molybdenum, bismuth, selenium, tellurium, zirconium, thorium, vanadium, germanium. This is also

true of titanium (N. 1). Furthermore, a small quantity of antimony (1–2 mgm.) dissolves. Phosphoric, arsenic, and vanadic acids are dissolved completely when tin, titanium, and zirconium are absent.

5. Aside from the elements named in N. 1, and under the specified conditions aside from those named in N. 3, no others are retained in the residue insoluble in HNO_3 in important quantity, as far as is known. Even the elements bismuth, tellurium, zirconium, and thorium, whose salts are readily hydrolyzed, dissolve completely when present alone in quantities up to 500 mgm. This is also true of zirconium, even when 500 mgm. Ti are present. The elements iron, aluminium, and chromium, whose oxides are made insoluble by ignition, dissolve completely when the residue has been heated only to 120°, at any rate upon the second digestion with HNO_3 (1.20). Of the element gold, if originally present as chloride, only the small portion reduced by dust from the air is left in the residue.

6. Whenever it is directed, as at the end of this procedure, to "wash" a residue or precipitate, it is understood, unless otherwise stated, that this operation is to be continued until the washings will give no test for some substance known to be present in the solution in considerable quantity.

Procedure 6. — Support the filter containing some of the residue insoluble in HNO_3 (P. 5) in a stout platinum ring or in a funnel completely covered with paraffine. Pour through it 5–10 ccm. pure concentrated HF, collecting the liquid in the platinum dish containing the main part of the residue. Heat on a steam-bath for 5 minutes. Dilute with 25 ccm. cold water, decant the solution through the same filter, and wash the residue and the filter thoroughly. Then rinse the residue from the platinum dish into a casserole. Collect the solution in a second platinum dish. (Residue, P. 7; solution, P. 31.)

Notes. — 1. The HF dissolves silica and all the oxides of the niobium and tungsten groups, except that of tin, when this is present in large quantity; but this also dissolves on diluting the solution with cold water. All the substances specifically named in P. 5, N. 3 also pass into solution in HF, with the exceptions of ThF_4 and $Th_3(PO_4)_4$, of the Bi_2O_3 present in excess of about 6 mgm., and of some $Sn_3(PO_4)_4$ when this is present in large quantity.

2. A residue undissolved by the HF may consist of one or more of the following substances, if the original substance was non-metallic: $PbSO_4$, $BaSO_4$, $SrSO_4$; HgS, native MoS_2; MnO_2, PbO_2; ignited or native Al_2O_3, Cr_2O_3, $FeCr_2O_4$ (chromite), SnO_2, or TiO_2; AgCl; BiF_3,

ThF_4; Prussian blue; $Sn_3(PO_4)_4$, $Th_3(PO_4)_4$ (as in monazite); certain silicates (such as cyanite, andalusite, tourmaline, beryl, zircon, topaz); S, C, SiC. It may consist of one of the following substances, if the original substance was a metal: Au; Pt, Ir, Rh, Ru, or Os, or alloys of these; or certain alloys of iron (such as ferrochrome, ferrosilicon).

3. In spite of the rather numerous exceptions named in the preceding note, by far the larger proportion of substances ordinarily submitted to analysis, including almost all silicates, are decomposed by treatment according to the foregoing procedures.

Procedure 7. — Add to the residue insoluble in HF (P. 6) 15 ccm. HCl (1.20), and boil gently for 5 minutes. Then add slowly 10 ccm. water, keeping the liquid at its boiling-point. Decant while still hot through the filter previously used, if this contains any of the residue. [If it is doubtful whether the HCl has dissolved anything, evaporate the solution to dryness to determine it.] If the residue has been dissolved to a considerable extent, but not completely, boil it with successive portions of HCl (1.20) as long as a considerable quantity of substance is dissolved, diluting and decanting each time as before. To the residue add 3 ccm. HNO_3 (1.42) and 10 ccm. HCl (1.20), and heat on a water-bath for 5 minutes, or longer if an action is taking place. Dilute with an equal volume of water, filter through the same filter-paper, and wash the residue. Unite the HCl and aqua regia solutions. Separate the residue from the filter, or incinerate the latter, if necessary. (Residue, P. 8; solution, P. 17.)

Notes. — 1. Of the substances named in P. 6, N. 2, which may constitute the undecomposed residue, it will be found that $PbSO_4$, $SrSO_4$, MnO_2, and PbO_2 dissolve completely in 30 ccm. HCl (1.20) on 5 minutes' boiling, even when such quantity is present as contains 500 mgm. of the metallic element; and they remain in solution on the addition of 20 ccm. boiling water. The same is true of fused AgCl up to a quantity containing 100 mgm. Ag, of $BaSO_4$ up to 20 mgm., and of $Sn_3(PO_4)_4$ in large quantity.

2. By the treatment with aqua regia, HgS, Au, and Pt (except when alloyed with another platinum metal) are also completely dissolved.

3. The cases in which a subsequent fusion must be resorted to are therefore rare. The important substances for which it is necessary are named in P. 8, N. 1 and 2.

Procedure 8. — If the residue insoluble in aqua regia (P. 7) is non-metallic and light-colored, and if it is thought to consist of a sili-

cate or of $BaSO_4$, or if there is no indication as to its nature, fuse it with Na_2CO_3 as directed in P. 9.

If the residue is non-metallic and light-colored, and if it is thought to consist of a metallic oxide, fluoride, or phosphate, fuse it with $K_2S_2O_7$ as directed in P. 12.

If the residue is metallic, or if it is non-metallic and dark-colored, fuse it with Na_2O_2 as described in P. 13.

Notes. — 1. The important light-colored non-metallic substances which may occur in the residue insoluble in HF, HCl, and aqua regia are: $BaSO_4$, certain silicates, ThF_4, native or ignited Al_2O_3, TiO_2, $ZrO_2.SiO_2$, monazite, and SnO_2. By fusion with Na_2CO_3 the silicates and $BaSO_4$ are readily converted into soluble compounds, but this method is ineffective with the other substances (except possibly ThF_4). All of these, except SnO_2, dissolve in dilute H_2SO_4 after fusion with $K_2S_2O_7$. SnO_2 is best brought into solution by fusing it with 20 times its weight of a mixture of equal quantities of Na_2CO_3 and S in a porcelain crucible, extracting the mass with water, and treating the solution according to Part II, and the residue, after dissolving in hot HCl (1.12) and properly diluting, by P. 71.

2. The important substances that may constitute a dark-colored non-metallic residue are: chromite ($FeCr_2O_4$), graphite or coal (C), carborundum (SiC), molybdenite (MoS_2), and Prussian blue ($Fe_4(FeC_6N_6)_3$). A metallic residue may consist of an alloy of iron (like ferrosilicon or ferrochrome) or of a platinum metal or alloy. Most of these substances require fusion with an oxidizing flux, and all of them yield to it. The extremely powerful one, Na_2O_2, is employed so that the method may be general; for even the platinum metals, if in a moderately fine state of division, are oxidized by it. A mixture of Na_2CO_3 and KNO_3 would effect decomposition of the other substances; and, if preferred, it may be substituted for Na_2O_2, except when platinum metals are to be treated.

Procedure 9. — If its character makes fusion with Na_2CO_3 advisable (P. 8), mix the residue insoluble in aqua regia (P. 7) with ten times its weight of anhydrous Na_2CO_3 in a platinum crucible. Cover the crucible and heat it for 30 minutes either over a powerful burner (preferably within a cylindrical porcelain jacket) or over a blast-lamp, adding more Na_2CO_3 if a perfectly fluid fusion does not result. Insert in the liquid mass a stout platinum wire with a small horizontal ring at the lower end, and allow the mass to solidify completely. Then heat the crucible till the mass begins to melt around the

sides, and remove it by means of the platinum wire. Digest it on a steam-bath with 50 ccm. water till the mass is entirely disintegrated. Filter, and wash the residue. (Residue, P. 10; solution, P. 11.)

Note. — 1. If the mass is not removed from the crucible, its disintegration by the hot water is often very slow.

Procedure 10. — Heat the residue from the aqueous solution of the fused mass (P. 9) with 5 ccm. HCl (1.12) for 5 minutes, and add 25 ccm. hot water. Filter, and wash the residue. (Residue, P. 12; solution, P. 71.)

Note. — 1. Of the elements of the tungsten, niobium, selenium, and silver groups, tin and titanium are the only ones that are at all likely to be present in the HCl solution of the fusion of the residue (P. 7) insoluble in all the acids. As these elements are tested for also in connection with subsequent groups, the solution is immediately precipitated with H_2S (P. 71).

Procedure 11. — Acidify the aqueous solution of the fused mass (P. 9) with HCl, evaporate the solution to dryness, and heat the residue in a hot closet at 120° for an hour. Heat the residue with 5 ccm. HCl (1.12). Add 25 ccm. water; filter; and wash the residue. (Residue, P. 6; solution, P. 71.)

Notes. — 1. The solution of the fused mass is evaporated with HCl, and the residue heated at 120° and treated with HCl to separate silica, which is very likely to be present. A white insoluble residue probably consists of nothing but silica; but, if desired, this may be determined by warming it with HF (P. 6), and treating the solution by the subsequent procedures (P. 31).

2. Since it is very improbable that elements of the selenium and silver groups are present, owing to the fact that most, if not all, of their compounds are decomposed by the preceding treatment with various acids, the solution of the dehydrated residue is precipitated at once with H_2S.

Procedure 12. — If the character of the residue insoluble in aqua regia (P. 7) makes fusion with $K_2S_2O_7$ advisable (P. 8), or if this residue has been fused with Na_2CO_3 and undecomposed substance still remains on treating the fused mass with HCl (P. 10), pour the residue gradually into a platinum crucible containing ten times as

much $K_2S_2O_7$ in a state of fusion. Cover the crucible, and keep the temperature at a dull red heat for 20 minutes. Cool the crucible, pour into it 2–4 ccm. H_2SO_4 (1.84) and heat again, keeping the crucible covered until the whole mass becomes fluid. Cool the crucible and gradually pour its (still liquid) contents into 30 ccm. water. Decant the solution from the residue, add to this 5–10 ccm. H_2SO_4 (1.20), and heat to boiling. Filter and wash the residue. (Residue, P. 6, and if there is still a residue, treat it by P. 20.) Unite the filtrate with the previously decanted solution. Add 2 drops HCl (1.12), shake the solution vigorously for 5 minutes with 1 ccm. moist precipitated Ag, and filter. (Precipitate, reject; filtrate, P. 71.)

Notes. — 1. The 2–4 ccm. H_2SO_4 are added at the end of the fusion to save the considerable time otherwise consumed in the disintegration of the mass by water, to dissolve as far as possible rare-earth phosphates (as in monazite) which otherwise may separate in large quantity on the addition of water, and to hold titanium in solution, which it does even though the solution be boiled. Any undissolved residue is heated with H_2SO_4 (1.20) in order to dissolve these phosphates and also any double sulphates of the rare-earths (like $2K_2SO_4.Th(SO_4)_2$) which may have been precipitated in crystalline form.

2. An insoluble residue may consist of SiO_2, which is ascertained by treating it with HF (P. 6) and evaporating the solution to complete dryness after the addition of a little H_2SO_4; of alkaline-earth sulphates, which are treated by P. 20; and of undecomposed substances (such as certain silicates, cassiterite, etc.), which would be left as a residue upon boiling with Na_2CO_3 (P. 20), and which should be fused with Na_2CO_3 (P. 9) or with a mixture of Na_2CO_3 and S (P. 8, N. 1).

3. The solution is first shaken with Ag to remove the platinum which is dissolved from the crucible by the acid flux; if this is not removed a precipitate will be obtained with H_2S even though no elements of that group are present. The Ag precipitate is rejected, since it cannot contain mercury (owing to its volatility at a red heat) or gold (owing to the metal being unattacked by $K_2S_2O_7$), and is very unlikely to contain palladium or platinum (aside from that taken up from the crucible), and since these are the only elements precipitable by silver from a solution containing little HCl (see Part IV).

Procedure 13. — If its character makes fusion with Na_2O_2 advisable (P. 8), introduce the residue insoluble in aqua regia (P. 7), gradually if a violent action occurs, into a nickel crucible in which

5 gm. Na_2O_2 have been brought to a state of fusion. Heat the lower part of the crucible to dull redness, maintaining a temperature sufficient to keep the mass fluid for from 5 to 20 minutes, according to the readiness with which the residue is attacked. After cooling, place the crucible on its side in a covered casserole, add 50 ccm. cold water, and, after the violent effervescence has ceased, warm gently. Rinse out the crucible, transfer the solution and residue to a flask, and add gradually HCl (1.20) until the black residue of $Ni_3O_4.2H_2O$ dissolves, meanwhile keeping the solution cold. If complete solution does not result, decant the solution, after settling, from the residue, boil the latter with HCl (1.20), and unite the solution and any residue with the decanted solution. Transfer the mixture to a 200 ccm. distilling flask, having its side arm bent downwards and dipping into 10 ccm. 5 % NaOH solution in an Erlenmeyer flask surrounded by a large beaker of cold water. Close the flask with a cork through which passes a straight tube reaching to the bottom. Boil the solution for 5–10 minutes, taking care that all the distillate condenses. Replace the NaOH solution containing the distillate by a fresh portion of NaOH solution, and distil again for 5 minutes. (Distillate, P. 14; residual solution, P. 15.)

Notes. — 1. Of the substances possibly present in a dark-colored or metallic residue, the platinum metals and their alloys are most difficultly attacked by Na_2O_2. They should therefore be rather finely powdered, which is usually best accomplished by pounding the substance in a diamond steel mortar. It is not necessary, however, to resort to the special methods of producing an extremely fine state of division, like fusion with lead, which have to be employed when other methods of attack, like heating with NaCl and Cl_2, are to be used. Twenty minutes' fusion is sufficient with 500 mgm. of the most resistant alloys.

2. As the nickel crucible is much attacked by the flux, the fusion should not be unduly prolonged. Silver and platinum crucibles are also strongly attacked, and have no advantage in this respect, while they have the disadvantage of being much more expensive.

3. The flux Na_2O_2 can now be obtained commercially in a fair degree of purity, being made from metallic sodium; it often contains some iron, however. Nevertheless, to determine the nature and approximate quantity of the impurities introduced from the crucible and flux into the solution to be analyzed, a blank fusion and an analysis of the fused mass should be made.

4. Upon treatment of the fused mass with water, a violent evolution of oxygen occurs, and a large quantity of a fine black precipitate consisting of $Ni_3O_4.2H_2O$ separates. This dissolves completely on the addition of HCl.

5. The products resulting from the fusion of the substances (named in P. 8, N. 2) possibly present in the residue, and treatment of the fused mass with water, are as follows: chromite, Fe_2O_3 and Na_2CrO_4; carbon, Na_2CO_3; carborundum, Na_2CO_3 and Na_2SiO_3; molybdenite, Na_2MoO_4 and Na_2SO_4; Prussian blue, Fe_2O_3 and Na_2CO_3; ferrosilicon or ferrochrome, Fe_2O_3 and Na_2SiO_3 or Na_2CrO_4; platinum, $xNa_2O.Pt_2O_3$; iridium, $xNa_2O.IrO_3$; rhodium, RhO_x (?); osmium, Na_2OsO_5 (?); ruthenium, Na_2RuO_5 (?). All of these products, except Fe_2O_3, $xNa_2O.Pt_2O_3$, $xNa_2O.IrO_3$, and RhO_x dissolve upon treating the fused mass with water. Na_2CrO_4 imparts to the solution a pure yellow color; Na_2OsO_5 a yellow-orange color; and Na_2RuO_5 a dark orange-red color. All of the products insoluble in water dissolve on the addition of HCl to the solution or on heating the residue with HCl (1.20), except a part of the $Pt_2O_3.2H_2O$ when present in large quantity. The $Pt_2O_3.2H_2O$ produced by action of the acid on $xNa_2O.Pt_2O_3$ forms a dense yellow powder, which is dissolved only slowly by hot HCl (1.20) or even aqua regia. $xNa_2O.IrO_3$ dissolves in HCl with production of a dark blue solution.

6. The solution must be kept cold during the neutralization, since otherwise osmium may be lost in the form of the very volatile OsO_4, which is formed when a Na_2OsO_5 solution is acidified. The solution must not be filtered through paper, as this immediately reduces Na_2RuO_5 with formation of a black deposit.

7. The OsO_4 (osmium tetroxide) set free when the Na_2O_2 solution is acidified distils over with great readiness (usually within two or three minutes), since in the pure state it boils not far from 100° and since it dissolves in water apparently without change. The vapor has an odor somewhat similar to that of chlorine, and is extremely irritating to the eyes and nose. The distillate assumes a yellow color when a little osmium; a dark orange color, when much osmium is present.

8. Although a similar volatile oxide of ruthenium (RuO_4) exists, it is not formed when the Na_2O_2 solution is heated with HCl; on the contrary, the Na_2RuO_5 present is reduced with formation of $RuCl_3$. Consequently no ruthenium distils over.

9. If osmium were present in the original substance in the form of one of its salts, it would be completely volatilized in the first treatment with HNO_3 (P. 1) or in the subsequent evaporation (P. 2 or 3); for all soluble osmium compounds yield OsO_4 when boiled with HNO_3. Therefore, if its presence in such a form be thought possible, the first treat-

ment of the substance with HNO_3 (1.20) should be carried out, as indicated in P. 1, in a distilling flask, the liquid boiled for 2 or 3 minutes, and the distillate collected as in this procedure and tested by P. 14. As osmium is in practice very rarely met with except in the metallic form, it is, as a general rule, unnecessary to complicate in this way the procedure for the preparation of the solution.

10. Since metallic osmium, both in the pure state and alloyed with iridium or other platinum metal, is scarcely attacked by aqua regia, unless it has been brought to an extremely fine state of division by a chemical method, there is little danger of completely dissolving and volatilizing it in the treatment with that solvent in P. 7. Still, if it is desired to determine with certainty the presence or absence of a small quantity of osmium, it is best either to heat the residue undissolved by HNO_3, HF, and HCl with the aqua regia in a distilling flask and to collect and test the distillate as in P. 13 and 14, or to fuse the residue with Na_2O_2 (as in P. 13) without treating it with aqua regia at all.

Procedure 14. — Add to the distillate (P. 13) 4–5 drops 20% $Na_2S_2O_3$ solution, acidify with HCl (1.12), keeping the liquid cool, and add to the solution one-fifth its volume of HCl (1.12). (Precipitate and solution, reject.)

Note. — 1. OsS_2 separates as a brownish-black precipitate. The test is obtained when only 0.5 mgm. Os is present in the solution submitted to distillation. It is the volatility of the osmium and its presence in the distillate that is especially characteristic — not the fact of its precipitating with $Na_2S_2O_3$; for if they could be present in the distillate, other elements, for example, ruthenium, would give a similar precipitate.

Procedure 15. — Evaporate the residual solution from the distillation (P. 13) to dryness, and heat the dry mass at 120° for an hour. Then heat it to boiling with 20 ccm. HCl (1.02). Filter, and wash the undissolved residue. (Residue, P. 16; solution, P. 71.)

Note. — 1. The solution is evaporated and the salt mass heated at 120°, so as to make insoluble the H_2SiO_3 and H_2WO_4 that may be present. PtO_3 may also be present in the residue undissolved by the HCl (1.02); see P. 13, N. 5.

Procedure 16. — Treat the residue (P. 15) just as described in P. 6. (Solution in HF, P. 31.) Add any residue undissolved by

HF to the HCl solution (P. 15), and treat the mixture by P. 71, allowing the cold solution saturated with H_2S to stand an hour or more before filtering.

Notes. — 1. Of the elements of the tungsten and niobium groups, only tungsten and titanium are at all likely to be present in this HF solution; for tin and antimony, even if present in the fused residue, would dissolve on treating the dehydrated residue with HCl (P. 15), and niobium and tantalum are not met with at all in alloys nor in compounds insoluble in HF. Hence, the procedure given for those groups may be shortened in its application to this HF solution, by the omission of those operations which serve only to remove and detect the elements almost certainly absent; or this HF solution may be united with the first HF solution obtained when the original dehydrated residue was treated with HF (P. 6).

2. The residue insoluble in HF, if of a yellow color, may consist of Pt_2O_3. It is added to the solution about to be precipitated with H_2S, because the reagent converts the Pt_2O_3 into Pt_2S_3, which dissolves when the H_2S precipitate is subsequently treated with aqua regia.

Procedure 17. — Evaporate the mixed HCl and aqua regia solutions of the residue insoluble in HNO_3 and HF (P. 7) just to dryness. Heat the residue to boiling with 10 ccm. HCl (1.02), cool, and after 2–3 minutes filter. Wash the undissolved residue thoroughly with as little HCl (1.02) as possible, adding the washings to the filtrate. (Precipitate, P. 18; filtrate, P. 71.)

Note. — 1. The residue undissolved by the HCl (1.02) may consist of AgCl, $PbCl_2$, $PbSO_4$, $BaSO_4$, and $SrSO_4$, which, though soluble in hot concentrated HCl, are only slightly dissolved by a small quantity of cold HCl (1.02). The solution may contain the other substances named in P. 7, N. 1 and 2, especially lead, manganese, mercury, gold, and the platinum metals. It is therefore united with the main solution and submitted to the regular scheme of analysis, beginning with the H_2S precipitation (P. 71).

Procedure 18. — Pour repeatedly through the filter containing the residue insoluble in dilute HCl (P. 17) a 10–15 ccm. portion of cold NH_4OH (0.90). Filter and wash the residue with NH_4OH (0.96). (Residue, P. 19.) Acidify the filtrate with HNO_3. (Precipitate and solution, reject.)

Note. — 1. The residue is treated with NH_4OH to extract any AgCl present. Cold NH_4OH is used, since $PbSO_4$ is somewhat soluble in hot NH_4OH. The filtrate is acidified to determine whether any silver is present. The AgCl dissolves in the NH_4OH, owing to the formation of a salt with a complex cathion, $Ag(NH_3)_2{}^{\cdot}Cl'$.

Procedure 19. — Pour repeatedly through the filter containing the residue undissolved by the NH_4OH (P. 18) a 10–20 ccm. portion of hot 25 % $NH_4C_2H_3O_2$ solution to which 5 % NH_4OH have been added. Filter and wash the residue with the $NH_4C_2H_3O_2$ solution until it is free from lead. (Residue, P. 20.) Acidify the filtrate with $HC_2H_3O_2$, and add a few drops of a 10 % K_2CrO_4 solution. (Precipitate and solution, reject.)

Note. — 1. The residue is treated with $NH_4C_2H_3O_2$ to extract any $PbSO_4$ or PbO_2H_2 present. Even 500 mgm. Pb as $PbSO_4$ dissolve in 15 ccm. boiling $NH_4C_2H_3O_2$ solution. $BaSO_4$ is not appreciably soluble. A small quantity of $SrSO_4$ dissolves, but this does not precipitate with K_2CrO_4 in the confirmatory test for lead. Even if all the $SrSO_4$ present in the residue passes into the NH_4OH solution, there is no danger of failing to detect strontium as a constituent of the original substance; for $SrSO_4$ is so soluble in dilute HNO_3 (P. 5) and dilute HCl (P. 17) that a considerable quantity of it will be found in the main solution; thus 10 ccm. of cold HCl (1.04) or of cold HNO_3 (1.032) saturated with $SrSO_4$ contain about 10 mgm. Sr.

Procedure 20. — Unite the residue insoluble in $NH_4C_2H_3O_2$ solution (P. 19) with the residue from the $K_2S_2O_7$ fusion (P. 12) after its treatment with HF. Transfer these, with the filters if necessary, to a casserole, add 10 ccm. saturated Na_2CO_3 solution, and boil gently for 10 minutes, replacing the water which evaporates. Dilute with an equal volume of water, and filter. (Filtrate, reject.) Wash the residue thoroughly, and pour repeatedly through the filter containing it a 10 ccm. portion of hot HCl (1.02). (Solution, P. 71.)

Notes. — 1. Even 500 mgm. Sr as $SrSO_4$ are completely converted to $SrCO_3$ by this procedure. An equal quantity of $BaSO_4$ would require boiling with two or three successive portions of Na_2CO_3 solution, but as the quantity of $BaSO_4$ that can be present in this residue cannot be very large, owing to its rather small solubility in HCl (1.20) (see P. 7, N. 1), a single boiling suffices.

2. The Mass-Action Law requires that the difficultly soluble sulphate be transformed into carbonate until the ratio (C_{SO_4}/C_{CO_3}) of the concentrations of the SO_4 and CO_3 ions in the solution becomes equal to the ratio (SP_{MSO_4}/SP_{MCO_3}) of the solubility-products of the sulphate and carbonate in pure water. Now since the second ratio, according to recent solubility determinations, has (at 18°) a value larger than 60 in the case of the two strontium salts, a very large amount of $SrSO_4$ would have to be transformed to Na_2SO_4 before the ratio C_{SO_4}/C_{CO_3} attained this value. On the other hand, in the case of the two barium salts, the second ratio has apparently the value 0.25 (since it is found that the conversion ceases when $C_{SO_4}/C_{CO_3} = 0.25$), so that after a certain amount of $BaSO_4$ has been transformed, the reaction ceases. Aside from this great difference in the equilibrium-ratios, the rate of transformation is doubtless much less in the case of the $BaSO_4$, owing to its very slight solubility. It is to increase this that the solution is boiled.

Confirmatory Experiments and References.

P. 1, N. 4. — The following minerals or products left a large residue when one gram was treated with HNO_3 (1.20) as above described: Galenite (PbS), emery (Al_2O_3), chromite ($FeCr_2O_4$), zircon ($ZrSiO_4$), pyrolusite (MnO_2), lead dioxide (PbO_2), cinnabar (HgS), fluorite (CaF_2), fused silver chloride (AgCl), and Prussian blue ($Fe_4(FeC_6N_6)_3$). One gram of fused $PbCrO_4$ dissolved on three successive digestions with 20 ccm. HNO_3 (1.20). One gram of precipitated $CaSO_4$ dissolved upon one treatment with 10 ccm. HNO_3 (1.20), after diluting with 20 ccm. water, and remained in solution upon cooling.

P. 3, N. 1. — In several experiments 500 mgm. Pb as $Pb(NO_3)_2$ were treated with 5 ccm. commercial HF containing some H_2SO_4. The mixture was then treated according to P. 3 and P. 5. A residue consisting of $PbSO_4$ always remained, as was proved by decomposing it with Na_2CO_3 and testing for its constituents.

3 ccm. pure 43% HF solution were mixed with 10 ccm. HCl (1.03) in one experiment and with 20 ccm. HCl (1.02) in another; then 1 ccm. 10% $BaCl_2.2H_2O$ solution was added; no precipitate (of BaF_2) separated even on standing 10 minutes. One drop (0.04 ccm.) H_2SO_4 (1.20) was then added: a precipitate formed immediately.

P. 3, N. 3. — To 5 ccm. portions of 43% HF solution 1% solutions of various elements were gradually added until a permanent precipitate was produced, waiting 2 or 3 minutes after the addition of each half milligram or milligram. The number of milligrams that had to be added were as follows: Li, 5; Mg, 2; Ca, 0.5; Sr, 8; Ba, 30; Pb, 0.5; Bi, 0.5; Th, 0.5; Ce, 0.5; Pr, 0.5; Nd, 0.5; La, 0.5; Y, 0.5; and Er, 0.5.

P. 3, N. 4. — 2 mgm. Ta as Ta_2O_5 were heated for 15 minutes on the water-bath with 5 ccm. 43% HF solution, and the solution was then evaporated to complete dryness, in one experiment twice with the addition of 2 ccm. HNO_3 (1.42), and in another, once without this addition. The residues were then tested for tantalum by the KHF_2 test as described in Part II. In the experiment in which the HNO_3 was added, a satisfactory test was obtained; in the other experiment, no test whatever was obtained, showing that the 2 mgm. Ta were completely volatilized in the latter case. 1 mgm. Ti as H_2TiO_3 was dissolved in 5 ccm. HF, and the solution was then evaporated to complete dryness, in one case twice with the addition of 2 ccm. HNO_3 (1.42), in another once without that addition. The residues were treated with 20 ccm. H_2O_2 and 2 ccm. HCl. No color was obtained in the former experiment; a color corresponding to at least 0.5 mgm. in the latter.

A mixture of 1 mgm. Se, 1 mgm. As, 1 mgm. Hg, and 1 mgm. Sb was evaporated to dryness with HNO_3 and treated according to P. 3 (without the addition of SiO_2) and subsequent procedures until the final tests for these four elements were reached. Very satisfactory tests for all of them were obtained, showing they were not volatilized in the HF evaporation.

About 40 mgm. GeO_2, made by heating the metal with HNO_3 (1.20) till it was dissolved, evaporating the solution to dryness, and heating the residue at 120° in a platinum dish to a constant weight, were treated with 5 ccm. HF and 5 ccm. HNO_3 (1.42); the solution was then evaporated to dryness and the residue heated to 120° and weighed: the change in weight was only 0.1 mgm.

P. 3, N. 5. — 100 mgm. Ta as Ta_2O_5 were dissolved in 5 ccm. HF and evaporated to dryness three times with 3 ccm. HNO_3 (1.42); the residue was then boiled with 15 ccm. HNO_3 (1.05) for 1 minute: the solution after filtration, neutralization with NH_4OH, and addition of $HC_2H_3O_2$ and $CaCl_2$ gave no precipitate, showing the absence of HF.

The same experiment was repeated with 100 mgm. Nb as Nb_2O_5 and with 100 mgm. Ti as H_2TiO_3 with just the same result.

P. 3, N. 6. — 50 mgm Ca as $Ca(NO_3)_2$ were digested on a water-bath 15 minutes with 5 ccm. HF; 5 ccm. HNO_3 (1.42) were added, and the solution was evaporated to complete dryness; the residue was covered with HNO_3 (1.42) and this was evaporated off; 10 ccm. HNO_3 (1.05) were then added; and the solution was made alkaline with NH_4OH: only a very slight turbidity resulted.

The same experiment was repeated several times with 200 and 500 mgm. Ca: in every case, a residue remained or a milky colloidal solution resulted upon treatment with HNO_3 (1.05).

500 mgm. Pb as $Pb(NO_3)_2$ and 500 mgm. Bi as $Bi(NO_3)_3$ were treated in separate experiments, in the manner just described: a perfectly clear solution was produced on adding the 10 ccm. HNO_3 (1.05).

A mixture of 250 mgm. Mg, 250 mgm. Ba, 250 mgm. Sr, and 250 mgm. Li was treated in the same manner; a perfectly clear solution resulted on the addition of the HNO_3 (1.05), and this gave no precipitate on neutralizing with NH_4OH and adding $HC_2H_3O_2$ and $CaCl_2$.

P. 3, N. 7. — In regard to the solubility in HF of the oxides of the tungsten and niobium groups, see C. E. on P. 6, N. 1.

P. 3, N. 8. — 500 mgm. Ca, as $Ca(NO_3)_2$, were treated according to P. 3 with addition of SiO_2, and then by P. 5 and 6: no residue whatever remained after the final treatment with HF. This experiment was repeated many times with the same result.

250 mgm. Y, 250 mgm. Ce, 500 mgm. Nd, a mixture of 50 mgm. Er and 50 mgm. Y, and a mixture of 500 mgm. Nd and 500 mgm. La (all as nitrates) were treated in separate experiments according to P. 3, 5, and 6: in all of these cases there was no residue or only a very small one (of 2–3 mgm.) after the final treatment with HF.

Portions of 250 mgm. Th, and of 50 mgm. Th, as $Th(NO_3)_4$, were treated according to P. 3, 5, and 6: on treatment with HF a dense crystalline residue estimated at one-tenth the original amount remained. This experiment was repeated many times with the same result.

P. 3, N. 11. — 100 mgm. Ta, as Ta_2O_5, were dissolved in 5 ccm. HF and evaporated to dryness three times with 3 ccm. HNO_3 (1.42); the residue was then boiled with 15 ccm. HNO_3 (1.05) for 1 minute: after filtration the solution gave a heavy precipitate with NH_4OH. The experiment was repeated with the modification that the residue was heated at 120° for 70 minutes after the three evaporations; the HNO_3 (1.05) solution then gave no precipitate whatever with NH_4OH. This shows that dehydration is necessary and sufficient to make the Ta_2O_5 insoluble.

The same experiment was twice made with 500 mgm. Sn: the HNO_3 solution of the residue which was not dehydrated gave a large precipitate with NH_4OH, and with H_2S (after evaporation with HCl).

P. 5, N. 1. — A series of experiments was made in which solutions of various elements were evaporated to dryness with HNO_3, and the residues were heated in a hot closet for one hour, and then boiled gently with 5 ccm. HNO_3 (1.20) for 5 minutes; the solutions thus obtained were diluted with 15 ccm. water, heated to boiling, filtered, and evaporated to dryness in crucibles, which were then gently ignited and weighed. It was found in this way that from a residue of 30 mgm. Sn, as H_2SnO_3, only 0.3 mgm. dissolved; from one of 70 mgm. W, as H_2WO_4, only 1.1 mgm. dissolved, which was proved to be not tungsten, but some impurity, by its complete insolubility in NH_4OH; from a residue of 56 mgm. Ta, as TaO_3H_3, only 0.4 mgm. dissolved; from one of 100 mgm. Nb a few milligrams dissolved, but on adding NH_4OH to the solution a precipitate formed which dissolved completely in

dilute HCl, proving that no niobium dissolved in the HNO_3; from a residue of 22 mgm. Sb, as Sb_2O_5, 1 mgm. Sb dissolved on the first treatment with HNO_3, and 0.9 mgm. on each of the two following treatments; and from a residue of 85 mgm. Ti, as H_2TiO_3, 8 mgm. dissolved.

750 mgm. metallic Sn were treated with HNO_3 (1.42), the acid was evaporated off, and the residue heated at 120° for an hour. The residue was then heated for ten minutes with 5 ccm. HNO_3 (1.20), 20 ccm. water added, the solution heated to boiling, and filtered. The filtrate was evaporated with HCl, and tested for tin by means of the $HgCl_2$ test. No tin was found to be present.

A mixture of 1 mgm. Ti, 1 mgm. Ta, 1 mgm. Nb, 1 mgm. W, 1 mgm. Sn, and 1 mgm. Sb was treated according to P. 3, 5, and 6, and the subsequent procedures (Part II) for the analysis of the tungsten and niobium groups. Distinct tests were obtained for all the elements except antimony, showing that their oxides remained in the residue insoluble in HNO_3. (See also T. A., Part II.)

2 mgm. Sb, as dehydrated Sb_2O_5, did not dissolve in 5 ccm. boiling HNO_3 (1.20); but it nearly disappeared upon adding 20 ccm. water and boiling. 5 mgm. Sb, as Sb_2O_5, treated in this way did not dissolve; but almost all of it dissolved upon a second treatment. 10 mgm. Sb left a large residue even after two treatments.

50 mgm. W, as Na_2WO_4, and 150 mgm. PO_4, as Na_2HPO_4, were evaporated with HNO_3 and heated at 120° for two hours; upon adding HNO_3 (1.20), and diluting, everything dissolved.

The same procedure was followed with a mixture of 5 mgm. W, as Na_2WO_4, and 50 mgm. As, as N_3AsO_4, with the same result.

10 mgm. W were precipitated as H_2WO_4 out of a Na_2WO_4 solution by boiling with HNO_3, and to the mixture 1 ccm. saturated $H_2C_4H_4O_6$ solution was added: the precipitate immediately dissolved.

50 mgm. Sb, as Sb_2O_5, after dehydration at 120° were treated in one experiment with 10 ccm. half-saturated citric acid solution, and in another experiment with 10 ccm. of a mixture of commercial lactic acid with its own volume of water; upon warming, the residue dissolved.

To 1 mgm. W, 1 mgm. Nb, 1 mgm. Ta, 1 mgm. Sn, 20 mgm. Sb (in separate experiments) in solution in 3–5 ccm. HF, 250 mgm. H_3BO_3 and 5 ccm. HNO_3 (1.42) were added. The solution was evaporated to dryness, and the residue treated with HNO_3 (1.20), which was then diluted with water. In each case, a small residue of the metallic oxide remained, and this did not go into solution on the addition of 500 mgm. more H_3BO_3.

To 1 gram H_3BO_3, 5 ccm. HF and 5 ccm. HNO_3 (1.42) were added, and the solution was evaporated to dryness on a water-bath; no residue was left.

A mixture of 500 mgm. Ti, as TiO_2, and 500 mgm. Zr, as $Zr(NO_3)_4$, was

dissolved in HF and evaporated to complete dryness four times. It was then heated at 120° for two hours. The residue was treated twice with HNO_3 and water according to the procedure. On the second treatment it went almost entirely into solution, showing that zirconium causes even large quantities of titanium to dissolve.

P. 5, N. 3. — 500 mgm. Mo, as MoO_3, were dissolved in HF, and following P. 3, the solution was evaporated three times with HNO_3 (1.42) and heated at 120° for an hour. The residue was twice heated with 5 ccm. HNO_3 (1.20), which was afterwards diluted with 20 ccm. water. After the two treatments about one-third of the molybdenum remained undissolved.

The experiment was repeated with 100 mgm. Mo. A fairly large residue remained after the first treatment of the dehydrated residue with HNO_3, but only a very small one (2–3 mgm.) after the second treatment.

In regard to Mo in presence of W or Sn, see T. A., Part II.

A mixture of 200 mgm. metallic Sb and 50 mgm. Bi, as $Bi(NO_3)_3$, was treated with HNO_3 (1.20), evaporated to dryness, and heated at 120°. The residue was heated 10 minutes with 5 ccm. HNO_3 (1.20), 20 ccm. water were added, and the mixture was heated to boiling and filtered. The residue was washed thoroughly with hot water and dissolved in HCl (1.20). To the solution NH_4OH and $(NH_4)_2S$ were added. Complete solution took place.

The experiment was repeated with a mixture of 500 mgm. Sb and 500 mgm. Bi. Even though the dehydrated residue was twice treated with HNO_3, and thoroughly washed with HNO_3 (1.05), a large black precipitate of Bi_2S_3 remained after adding NH_4OH and $(NH_4)_2S$ to the HCl solution of the HNO_3 residue.

A mixture of 50 mgm. Se, as SeO_2, and 200 mgm. Sb, as $SbCl_3$, was evaporated three times with HNO_3 and the residue heated at 120°. It was then treated with HNO_3 and water in the usual manner, and thoroughly washed with water. The undissolved residue was treated with HF, HCl, and H_2SO_3. The black precipitate which separated was boiled with HNO_3, the solution distilled with HBr, and the distillate treated with H_2SO_3. A red precipitate of Se, amounting to perhaps 5 mgm., separated.

In regard to ThF_4, see C. E. on P. 3, N. 8.

GeO_2 was made by heating the metal with HNO_3 (1.42), evaporating with HF and then with HNO_3, and dehydrating at 120°; the residue, which then weighed 110 mgm., was boiled 1 minute with 5 ccm. HNO_3 (1.20), then 20 ccm. water were added, the mixture was boiled again and filtered, and the filtrate was evaporated and the residue heated at 120° and weighed; it weighed 89 mgm., showing that 21 mgm. had dissolved. This residue of 89 mgm. was then treated again in the same manner; this time 28.5 mgm. dissolved.

50 mgm. Se, as SeO_2, and 200 mgm. metallic Sn were treated in the same manner, except that the residue insoluble in HNO_3 was dissolved in HBr, the

solution distilled and the distillate treated with H_2SO_3 and KI; a large red precipitate of Se (of perhaps 10 mgm.) was obtained.

50 mgm. Te, as TeO_2, with 200 mgm. metallic Sn in one experiment and with 200 mgm. Sb, as $SbCl_3$, in another, were treated in the same manner, except that the residue insoluble in HNO_3 was dissolved in HF, the solution evaporated with HCl and treated with H_2SO_3; a large black precipitate of Te formed in each case.

In regard to Se and Te in presence of elements of the tungsten and niobium groups, see also T. A., Part II.

50 mgm. Zr, as $Zr(NO_3)_4$, with 600 mgm. PO_4, as Na_2HPO_4, in one experiment and with 800 mgm. As, as As_2O_3, in another, were evaporated with HNO_3 and the residue heated at 120°. On treatment with HNO_3 (1.20) and dilution, a large residue remained and the solution gave a large precipitate with NH_4OH, showing that the zirconium divided itself between the two.

The experiment was repeated with a mixture of 500 mgm. Zr and 50 mgm. As: scarcely any residue remained after the treatment with HNO_3.

The last experiment was repeated, substituting 500 mgm. Ti dissolved in HF for the 500 mgm. Zr. The HNO_3 extract of the residue, after evaporation with 1 ccm. H_2SO_4, gave, upon addition of one-fifth its volume of HCl (1.12) and saturation for one hour at the boiling temperature, a considerable precipitate of As_2S_5. The residue after similar treatment also yielded a precipitate of As_2S_5 which was somewhat smaller than that obtained from the solution, showing that arsenic divides itself between the residue and solution when titanium is present.

250 mgm. Th, as $Th(NO_3)_4$, and 250 mgm. PO_4, as Na_2HPO_4, were evaporated with HNO_3 and heated at 120° for two hours. On heating on a water-bath with 10 ccm. HNO_3 (1.20), everything dissolved except a few hard particles. On adding 20 ccm. cold water a large flocculent precipitate formed, and upon then heating on the steam-bath the solution gelatinized.

50 mgm. V (as $(NH_4)_3VO_4$) and 500 mgm. Sn (as $SnCl_2$) were evaporated repeatedly with HNO_3, and the residue was heated at 120° and then treated with HNO_3 (1.20). A bright yellow residue remained, which upon treatment with HCl (1.20) yielded a blue-green solution; and the HNO_3 solution was of a brown color; thus showing that the vanadium was divided.

P. 5, N. 4. — See C. E. on P. 3, N. 3, and T. A., Part II.

P. 5, N. 5. — 500 mgm. Zr, Th, Te, Bi, Al, Cr, Pb and 75 mgm. Ga, as nitrates, were, in separate experiments, evaporated to dryness with HNO_3, and the residue heated for an hour at 120°; this was then heated with 5 ccm. HNO_3 (1.20) and finally with 20 ccm. water: everything dissolved in this single treatment; the gallium did not do so, however, until the 20 ccm. water were added. The experiment was repeated with 500 mgm. V, as $(NH_4)_3VO_4$, dissolved in HF, and with 500 mgm. Fe, as $FeCl_3$: two treatments of the

dehydrated residue with HNO_3 and water were necessary and sufficient to produce complete solution.

A mixture of 500 mgm. Ti, as TiO_2, and 500 mgm. Zr, as $Zr(NO_3)_4$, was dissolved in HCl, and the mixture evaporated three times with the addition of HNO_3 (1.42), and then heated at 120° for two hours. The residue was treated twice according to the procedure with HNO_3 (1.20) and water, and the residue still remaining was dissolved in HF, the solution evaporated with 1 ccm. H_2SO_4 (1.84), and then diluted with 100 ccm. H_2O_2, and 1 ccm. Na_2HPO_4 was added. No precipitate of $Zr_3(PO_4)_4$ separated on 20 minutes' standing.

A mixture of 50 mgm. each of Al, Ni, V, Cr, Be, and Zr was treated in the manner just described: everything dissolved on the first treatment with HNO_3.

The C. E. on P. 3, N. 8, made with the rare-earth elements other than thorium, show that even large quantities of these dissolve completely upon the treatment with the HNO_3.

20 mgm. Au, as $AuCl_3$, were four times evaporated with a little HNO_3 (1.42) and then heated at 120° for two hours. On heating with 5 ccm. HNO_3 (1.20), all but 2–3 mgm., consisting of a metallic powder, dissolved.

P. 6, N. 1. — 500 mgm. Sn, as metal, of Sb, as metal, of W, as Na_2WO_4, of Ti, as TiO_2, of Mo, as MoO_3, of Te, as TeO_2, and 30 mgm. Ge, as GeO_2, were treated in separate experiments with HNO_3, the liquid evaporated off, the residue heated at 120° for an hour or more and then heated on a steam-bath for 5 minutes with 5–10 ccm. HF: a clear or slightly opalescent solution resulted in every case except that of tin. 20 ccm. cold water were then added to each solution: the tin solution became clear, and all the others remained so.

To 5 ccm. HF, diluted with 25 ccm. cold water, a 1% Bi solution was added, 1 mgm. Bi at a time, until a permanent precipitate formed: 6 mgm. Bi were required.

To a HF solution of 500 mgm. Sn, as SnO_3H_2, 400 mgm. PO_4, as Na_2HPO_4, were added, the mixture evaporated to dryness three times with HNO_3, and the residue heated an hour at 120°; then it was heated with 5 ccm. HF, and finally 20 ccm. water were added: a large residue of at least 100 mgm. remained, and this did not dissolve on a second treatment with HF and water.

See also C. E. on P. 6, N. 3, in those cases where the minerals contain the elements of the tungsten and niobium groups.

P. 6, N. 2. — One gram of each of the following substances was treated according to P. 1, 3, 5, and 6, with the result that a large residue was left on the final treatment with HF: galenite (PbS), cinnabar (HgS), molybdenite (MoS_2), pyrolusite (MnO_2), lead dioxide (PbO_2), emery (Al_2O_3), chromite ($FeCr_2O_4$), cassiterite (SnO_2), rutile (TiO_2), fused silver chloride (AgCl), cy-

anite (Al_2SiO_5), tourmaline (Al_2O_3, (Fe, Mn, Mg)O, (K, Na, Li)$_2$O, B_2O_3, SiO_2, F), beryl ($Be_3Al_2Si_6O_{18}$), zircon ($ZrSiO_4$), monazite ($(Ca, La, Pr)_{15}(PO_4)_{10}Th_2P_2O_9$).

That andalusite and cyanite (Al_2SiO_5) and tourmaline are not decomposed by HF is stated by Jannasch in his *Gewichtsanalyse*, 231, 233 (1897).

P. 6, N. 3. — One gram of each of the following substances in the form of an impalpable powder was treated according to P. 1, 3, 5 and 6, with the result that no residue, or only a very small one amounting to 1–5 mgm., was left on the final treatment with HF: magnetite (Fe_3O_4), menaccanite ($FeTiO_3$, Fe_2O_3), pyrite (FeS_2), pyrrhotite (Fe_7S_8), chalcopyrite ($CuFeS_2$), stibnite (Sb_2S_3), niccolite (NiAs), fluorite (CaF_2), cryolite (Na_3AlF_6), gypsum ($CaSO_4$), wollastonite ($CaSiO_3$), tremolite ($(Ca, Mg)SiO_3$), titanite ($CaTiSiO_5$), orthoclase ($K_2Al_2Si_6O_{16}$), labradorite ((Ca, Na_2) $Al_2Si_3O_{10}$), garnet ($(Ca, Mg, Mn, Fe)_3Al_2Si_3O_{12}$), gadolinite ($(Y, Ce, Be, Fe)_3SiO_5$), scheelite ($CaWO_4$), columbite ($Fe(Nb, Ta)_2O_6$), samarskite ($(Fe, Y, VO_2)_5$ $(Nb, Ta)_4O_{15}$), and the rocks basalt, obsidian, amphibole, and lava.

P. 7, N. 1. — To 500 mgm. Pb, as $PbSO_4$, successive portions of 5 ccm. HCl (1.20) were added, the solution being boiled after each addition, until the solid all went into solution: 30 ccm. sufficed to produce this result. 90 ccm. water were then gradually added, keeping the solution at the boiling point: no precipitate was produced. 800 mgm. Pb, as PbO_2, dissolved readily in 30 ccm. HCl (1.20) and remained in solution on adding 90 ccm. water.

To 20 mgm. $BaSO_4$ 30 ccm. HCl (1.20) were added and the liquid boiled a few minutes: complete solution resulted. 30 ccm. water were added to the solution kept at the boiling point: no precipitate formed.

The same experiment was repeated with 100 mgm. AgCl with the same result.

500 mgm. fused AgCl in the form of shavings were boiled for 3 or 4 minutes with successive 30 ccm. portions of HCl (1.20): the solid all dissolved on the third treatment or in 90 ccm. HCl (1.20).

500 mgm. Sn, as metal, and 400 mgm. PO_4, as Na_2HPO_4, were evaporated with HNO_3 (1.42) and heated at 120°; the residue was treated twice with HF and water, as described in P. 6, and the large residue still remaining (amounting apparently to 200 mgm.) was heated on a steam-bath for 10 minutes with 15 ccm. HCl (1.20): complete solution occurred.

P. 7, N. 3. — The following substances, in the form of a fine powder, were submitted, if non-metallic, in quantity of 1 gm. to P. 1, 3, 5, 6, and 7; if metallic, in quantity of 0.5 gm. to P. 4, 5, 6, and 7, with the result that a large residue, amounting to at least one-half of the original substance, remained in every case: molybdenite (MoS_2), emery (Al_2O_3), chromite ($FeCr_2O_4$), cassiterite (SnO_2), rutile (TiO_2), thorium fluoride (ThF_4), Prussian blue ($Fe_4(FeC_6N_6)_3$), cyanite (Al_2SiO_5), tourmaline, zircon ($ZrSiO_4$), monazite

(mainly $Th_3(PO_4)_4$), metallic rhodium (Rh), metallic iridium (Ir), Ural Mts. platinum ore (Pt, Pd, Os, Ir), Ural Mts. osmium-iridium (Os, Ir), crude ruthenium (Ru), ferrochrome (Cr, Fe), ferrosilicon (Fe with 13% Si).

P. 8, N. 1. — Barium sulphate, tourmaline, cyanite, and allied silicates are analyzed quantitatively by decomposition with Na_2CO_3. See Classen, Quantitative Analysis, Harriman's translation, p. 62, 204.

330 mgm. of cyanite, constituting the residue left after treatment of 1 gm. of the mineral by P. 1, 3, 5, and 6, were fused with 7 gm. Na_2CO_3 (this large quantity being necessary to produce a fluid fusion); on treatment first with hot water, and then with HCl, everything dissolved.

One gram of each of the following substances as an impalpable powder was treated by P. 1, 3, 5, 6, and 7, and the residue was fused with Na_2CO_3 as directed in P. 9: emery (Al_2O_3), rutile (TiO_2), cassiterite (SnO_2), monazite ($Th_3(PO_4)_4$, etc.), and zircon ($ZrSiO_4$). A large residue was left upon extracting the fusion with water and adding HCl to the residue (P. 10, 11).

The residues undecomposed by Na_2CO_3, obtained in the preceding experiment, were fused with $K_2S_2O_7$ by P. 12: emery, rutile, zircon, and monazite went completely into solution on adding the fusion to water, or upon treating the residue with H_2SO_4 (1.20). In the case of cassiterite, a large residue (450 mgm.) was left undissolved.

P. 8, N. 2. — 500 mgm. of each of the following substances, reduced to a fine but far from impalpable powder, were first treated for from 10 to 30 minutes with strong aqua regia, and the residues were then introduced into a nickel crucible containing 5 gm. Na_2O_2 in a state of fusion, and the fusion was maintained for from 5 to 20 minutes: molybdenite (MoS_2), carborundum (SiC), ferrosilicon (Fe with 13% Si), ferrochrome (Fe xCr), Ural Mts. platinum ore, Ural Mts. osmium-iridium, pure metallic iridium, crude metallic ruthenium, and (100 mgm.) pure metallic rhodium. All of these substances except the platinum metals reacted violently with the Na_2O_2, with the production of much light and heat. Complete solution resulted in case of all the substances upon adding to the fused mass 75 ccm. water, neutralizing with HCl, adding a moderate excess of it and heating (except that in case of carborundum a small flocculent precipitate of SiO_4H_4 separated).

P. 12, N. 1. — One gram monazite was treated with HF and HNO_3 (P. 2 and 5), and the residue was fused with $K_2S_2O_7$ and H_2SO_4 (P. 12). On adding the mass to water, a flocculent precipitate formed; but this dissolved on decanting the liquid and adding 10 ccm. H_2SO_4 (1.20).

500 mgm. Ti, as TiO_2, were fused with 5 gm. $K_2S_2O_7$ and 4 ccm. H_2SO_4 were added. On adding the mass to 50 ccm. water everything dissolved, and remained in solution upon boiling.

10 gm. $K_2S_2O_7$ were heated at a dull red heat in a covered platinum crucible for 20 minutes. The mass was cooled, 2 ccm. H_2SO_4 (1.84) were

added, and the mixture heated for 15 minutes below its boiling point till a clear fusion resulted. On cooling, about half the mass separated as a compact solid and the other half remained viscous. On adding 2 ccm. more of H_2SO_4 (1.84), reheating for 10 minutes till a clear fusion was obtained, and then cooling, the mass became viscous, but was so liquid that it could be poured out.

P. 12, N. 3. — The liquid mass obtained in the last experiment was added to 30 ccm. water, two drops HCl (1.20) added, and the solution was then shaken with 1 ccm. Ag. From the color of the precipitate it was estimated by comparison with the colors obtained with known amounts of platinum, that 2 mgm. Pt had been taken up from the crucible.

P. 13, N. 1. — See C. E. on P. 8, N. 2, in regard to action of Na_2O_2 on the substances that may be present in a dark-colored or metallic residue.

P. 13, N. 2. — 5 gm. Na_2O_2 were fused at a lower red heat for 20 minutes in a 35 ccm. nickel crucible weighing 17 gm. The crucible, after washing out and drying, had lost 1.0 gm.

2 gm. Na_2O_2 were fused for 20 minutes on a silver crucible cover: the cover lost 0.9 gm.

In regard to the action of Na_2O_2 on Ni, Fe, Ag, and Pt, see also Dudley, *Am. Chem. J.*, **28**, 59–66 (1902), and Leidié and Quennessen, *Bull. soc. chim.* (3) **27**, 179–183 (1902).

P. 13, N. 3. — 5 gm. Na_2O_2 from Roessler and Hasslacher, N. Y., made from metallic sodium under the Castner patent, was submitted to a qualitative analysis. This quantity contained only about 3 mgm. Fe and 1 mgm. Sb as metallic impurities.

P. 13, N. 4. — For the composition of the hydrated oxide of nickel produced, see Dudley, *J. Am. Chem. Soc.*, **18**, 901–902 (1896).

P. 13, N. 5. — For the composition of the fusion-products of platinum, see Dudley, *Am. Chem. J.*, **28**, 59–66 (1902); of iridium, Claus, *J. prakt. Chem.*, **39**, 101 (1846).

500 mgm. Ir, as metal, and 500 mgm. Pt, as metal, were in separate experiments fused in a nickel crucible with 5 gm. Na_2O_2 for 75 minutes. The fused mass was treated with 100 ccm. water, and the coal-black residue allowed to settle. The very slightly yellowish solution was decanted, acidified with HCl, and evaporated nearly to dryness; the residue was treated with HCl (1.20); the solution was decanted from the pure white NaCl and evaporated to dryness with HNO_3; the residue was dissolved in 1 ccm. water, and the solution was saturated with NH_4Cl. In the case of the iridium, only about $\frac{1}{2}$ mgm. Ir separated as a black precipitate, showing that the fusion-product was almost insoluble in water. This is in disagreement with the statement of Leidié and Quennessen, *Bull. soc. chim.* (3), **27**, 181 (1902), according to which the iridium after fusion dissolves completely in water with production

of a deep blue solution. In the case of the platinum, no $(NH_4)_2PtCl_6$ was obtained. The residue insoluble in water was thoroughly washed, and it was then warmed with HCl (1.20). In the case of the iridium it very quickly dissolved to a clear dark blue solution, which during evaporation changed to a dark red color, In the case of platinum, a large quantity of a dense yellow residue remained after long boiling with HCl (1.20) and strong aqua regia. The HCl solution, however, contained a large quantity of platinum, as was shown by precipitating it in a pressure bottle with H_2S.

500 mgm. crude Ru were fused with 5 gm. Na_2O_2 and treated with water in the usual manner. The aqueous solution was dark orange-red, and upon adding HCl to the solution and residue, a clear, very dark red solution resulted.

100 mgm. commercial Rh were fused with Na_2O_2 and treated with water. The supernatant liquid after the precipitate settled was dark orange-yellow, and it remained so after decanting and acidifying with HCl, but it became colorless on boiling; these results being perhaps attributable to the presence of osmium. The black residue and adhering solution were treated with HCl: in the cold there was a large, finely divided cream-colored residue, but upon heating this almost entirely dissolved, yielding a dark yellow-orange solution.

P. 13, N. 7. — 200 mgm. Os were fused with Na_2O_2, the fused mass treated with water and HCl, and the liquid distilled (as in P. 13): after distilling 5 minutes, the dark orange distillate was replaced by fresh NaOH; after distilling 3 minutes longer, a yellow distillate corresponding in color to that given by 4–5 mgm. was obtained; on again replacing the distillate and boiling for 2 or 3 minutes longer, a colorless distillate giving no precipitate with $Na_2S_2O_3$ and HCl resulted. 25 ccm. HNO_3 (1.42) were then added to the residual solution, and the distillation continued for 10 minutes; the light yellow distillate was then treated with HCl and 2 ccm. saturated $Na_2S_2O_3$ solution: the precipitate obtained was pure white, showing that the osmium distilled over completely in less than 10 minutes and that the addition of HNO_3 is unnecessary.

P. 13, N. 8. — 500 mgm. crude Ru were fused with Na_2O_2, the fused mass treated with water and HCl, and the liquid distilled (as in P. 13): a weakly colored distillate, giving with HCl and $Na_2S_2O_3$ a small precipitate corresponding to 1–2 mgm., was obtained; this was probably due to a little osmium present in the material used. On further distillation into a new portion of NaOH, the latter remained colorless, showing that the ruthenium does not distil over.

P. 13, N. 10. — In one experiment 200 mgm. very finely powdered osmium, and in another 500 mgm. powdered osmium-iridium, were boiled in a distilling flask with strong aqua regia, and the distillate caught in NaOH solution: in neither case did the distillate give a dark-colored precipitate when tested with $Na_2S_2O_3$ and HCl.

P. 14, N. 1. — That the distillation and test with $Na_2S_2O_8$ will show 0.5 mgm. Os was proved by experiment.

The distillate obtained by distilling 1 mgm. Ru with dilute H_2SO_4 and $KMnO_4$ was tested with $Na_2S_2O_8$ by P. 14. A black precipitate was produced.

P. 16, N. 2. — The dense yellow residue of Pt_2O_8 insoluble in HCl and aqua regia, referred to in C. E. on P. 13, N. 5, was allowed to stand in the cold over night under water saturated with H_2S: it was completely converted to a black sulphide, which dissolved readily in aqua regia.

P. 18, N. 1. — As to the solubility of AgCl in NH_4OH, see Bodländer and Fittig, *Ztschr. phys. Chem.*, **39**, 602 (1901); Whitney and Melcher, *J. Am. Chem. Soc.*, **25**, 78 (1903).

500 mgm. Pb, as $PbSO_4$, were boiled with 20 ccm. NH_4OH (0.90), the mixture filtered hot, the filtrate nearly neutralized with HNO_3, and then acidified slightly with $HC_2H_3O_2$, and a few drops of K_2CrO_4 added: a considerable yellow precipitate of $PbCrO_4$ formed. The experiment was repeated with the modification that the NH_4OH solution was cooled before filtering: in this case a precipitate equivalent to only about 0.2 mgm. Pb resulted.

P. 19, N. 1. — The statement as to the quantity of $PbSO_4$ dissolved by 15 ccm. $NH_4C_2H_3O_2$ solution is based on a direct experiment.

A mixture of 500 mgm. Ba and 500 mgm. Sr, freshly precipitated as $BaSO_4$ and $SrSO_4$, was collected on a filter, a portion of 10 ccm. hot $NH_4C_2H_3O_2$ reagent was poured several times through the filter, the filtrate was acidified with $HC_2H_3O_2$, and a few drops of K_2CrO_4 were added: no precipitate resulted.

500 mgm. Sr, as $SrSO_4$, were boiled with 20 ccm. of the $NH_4C_2H_3O_2$ reagent, filtered while hot, and 30 ccm. of $(NH_4)_2CO_3$ added: after standing for 10 minutes, a precipitate estimated at 3–5 mgm. had separated.

For the solubility of $SrSO_4$ in HCl (1.04) and HNO_3 (1.032) see Fresenius, *Quantitative Analysis*, Am. Ed. of 1881, p. 815.

P. 20, N. 1. — 500 mgm. Sr, as freshly precipitated $SrSO_4$, were boiled for 10 minutes with 10 ccm. saturated Na_2CO_3 solution, the precipitate washed, and then treated with 10 ccm. cold HCl (1.12): it entirely dissolved.

500 mgm. Ba, as freshly precipitated $BaSO_4$, were boiled for 5 minutes with 25 ccm. saturated Na_2CO_3 solution; the solution was then decanted and the residue boiled for 5 minutes with 10 ccm. Na_2CO_3 solution; the solution was again decanted, the residue washed and treated with 10 ccm. HCl (1.02): it dissolved completely.

P. 20, N. 2. — For the theory of the equilibrium between two difficultly soluble salts in the presence of soluble ones with common ions and the results in the case of $BaSO_4$ and $BaCO_3$, see Nernst, *Theoretische Chemie*, 3d Ed., p. 498.

As to the solubility of $BaSO_4$, $BaCO_3$, $SrSO_4$ and $SrCO_3$ in water, see Kohlrausch and Rose, *Ztschr. phys. Chem.*, **12**, 241 (1893). It should not be forgotten, however, that the values given in the cases of the carbonates are much higher than correspond to the true solubility-products, owing to the effect of hydrolysis.

THE COMPOSITION OF SEWAGE IN RELATION TO PROBLEMS OF DISPOSAL.

By GEORGE W. FULLER.

Read March 26, 1903.

It is about fifty years ago that the first systematic analyses of sewage were undertaken in order to throw light upon problems of sewage disposal. From time to time it is well to review the progress made in fields of applied science in order to appreciate the relative advances in different branches of a subject, and especially to note wherein efforts towards improved conditions may be most fruitfully made.

In the middle of the last century the subject of sewerage and sewage disposal was practically in its infancy, and surrounded with many dissensions and uncertainties. The removal of municipal wastes by water carriage underground had been undertaken at London and a few other places, but very little progress in the development of this branch of public works had been made. In fact, London had just passed through the transitional stages whereby connections from the houses to the underground water channels were first prohibited, then permitted, and finally made compulsory by law.

The sewers themselves in those days were very crude affairs, and poorly designed as to alignment, size, slope, and velocities.

The disposal of sewage other than by discharging it into the nearest water course was very exceptional, although at the Craigentinny Meadows near Edinburgh and at Bunzlau, Prussia, sewage had been used for irrigation purposes since the middle of the eighteenth century. Numerous discussions were taking place as to the commercial value of sewage for fertilizing purposes, and of the means of taking advantage of the money value of sewage for this use. Hundreds of patented processes for the treatment of sewage were announced, most of which involved the use of some one or more of nearly all the chemicals which could then be made upon a commercial scale.

Largely through the efforts of several commissions and sanitary authorities in Great Britain, the next twenty-five years, or the third quarter of the last century, saw great progress made abroad regarding improved sewerage. At the end of that period, fundamental principles controlling the design of sewers were well understood by a considerable number of persons who had specially studied the matter; and efficient sewerage systems existed in various European cities, and in a few instances in this country. The last quarter of the century was characterized by wide dissemination of the knowledge and practice of sewer construction, until at present there are comparatively few cities and large towns which are not fairly well equipped in this respect.

Regarding sewage disposal, the situation in some respects has been and is different. In some instances this feature is so simple that it takes care of itself; in others there is no difficulty in applying sewage to land readily and economically; but in some cases, where cities are situated on relatively small streams, efficient sewage disposal has been and still is a difficult and expensive undertaking.

The disposal of sewage in relatively large volumes of water by dilution is still the prevailing method of disposal. Where purification processes are required, the practicability of irrigation and of intermittent filtration through areas of porous sand is well known. As to chemical precipitation, which has been so generally practiced abroad during the past generation, and where more than two hundred plants are now in operation, the time has come when the limitations to its merits are much more clearly recognized than formerly. To remove practically all of the suspended matters and one-half of the organic matter from sewage and to discharge the effluent into relatively small water courses is no longer permissible in numerous places abroad, and in this country instances are becoming more and more frequent where inland towns and cities must seek means for a substantially complete removal of decomposing matters before the sewage is discharged into small streams.

In Massachusetts, where relatively large areas of porous land are near at hand at moderate cost, and where sanitary matters are supervised with such eminent skill as is shown by the Massachusetts State Board of Health, these matters are not ordinarily of perplexing moment. In the South and West, however, where the glacial drift formation with its porous sand is absent, the interest is much keener in the

progress which is being made in a practical way in methods for the treatment of sewage by plants of artificial construction, occupying areas only a small fraction of that necessary for intermittent filtration. In the last ten to fifteen years, through the careful studies of the Massachusetts State Board of Health, and later by various authorities in England, progress in this direction has been made rapidly, at least so far as relates to the evidence which may be accumulated on a small, experimental scale.

As to the influence of various factors which affect the efficiency and cost of the so-called "rapid" methods of sewage treatment, the information as to results which may be expected from operations on a large scale is not so well crystallized as might be desired; and in fact is far less precise in its nature than that which relates to the purely constructive features of the collecting sewers to gather the sewage and convey it to the point of treatment.

In some ways the absence of crystallized evidence regarding these processes of sewage treatment depends upon matters of an analytical nature, dealing with the composition of sewage. This field is a very broad one, and it is not the purpose here to attempt to discuss it, but rather to point out a few ways in which more accurate information concerning the composition of sewage may perhaps facilitate progress in disposing of sewage so as to prevent nuisances from the bad odors resulting from putrefaction, which takes place when bodies of water are overcharged with polluting matters. No attempt is made here to consider that aspect of sewage disposal which deals with the infection of bodies of water by sewage, although it may be mentioned in passing that the literature upon this aspect of the subject needs thorough overhauling, in order that the matter shall be placed upon a more sound and practical basis than prevailing views indicate. In this latter task, laboratory men have important work to perform.

Strictly speaking, sewage disposal as referred to in this paper relates particularly to the dilution method, to modes of treatment preparatory to filtration, and to those so-called biological methods in which rapid rates of filtration are employed. No reference of a descriptive nature is made to these processes, which are doubtless well known to most of you, and which have been well outlined in recent articles by Professor Kinnicutt.

Among the fundamental principles associated with these sewage disposal problems may be noted the following:

1. The limitation in the amount of sewage which may be discharged into a water course without putrefaction setting in depends upon the oxygen-consuming properties of the sewage measured against the oxygen in the water of the stream, after making due allowance for the consumption of oxygen by the constituents of the water and by the matters contained on the bottom and sides of the stream.

2. Where it is necessary to filter sewage through beds of artificial construction it is highly advantageous to give the sewage a preparatory treatment by which there is removed a large portion of the matters suspended in the raw sewage. In order to make feasible high rates of filtration this is just as important as it is to afford a preliminary treatment to the muddy waters of the South and West prior to their filtration in a system of water purification works.

3. The rate of filtration which is permissible for sewage filters bears an inverse relation to the amount of organic matter contained in the applied liquid, other things being equal.

Each of these propositions is, of course, a large theme in itself. The purpose of this paper, as already indicated, is solely to refer to them in an illustrative sort of way in order to make plain, if possible, the significance which the composition of sewage, accurately known, bears to these important matters.

To the engineer who has to design artificially constructed purification works, and estimate the cost of their operation, it will be seen at a glance that it is highly desirable to know approximately the amount of suspended matter which on an average may be expected to be contained in the sewage before and after it has passed through various preparatory treatments. It is also important to know the amount of organic matter in the sewage to be applied to the filters in order to estimate a proper rate of treatment. This information as to organic matter is also essential in estimating approximately the amount of sewage that may be applied under given conditions to a stream with a certain flow without the putrefactive processes becoming a nuisance.

Here in Massachusetts, through the admirable equipment of the State Board of Health, these problems can be readily and safely solved as they present themselves. To one who has to deal with disposal problems in some other sections, the conditions are likely to be radically different, and the amount of detailed local data which may be obtained to serve as a guide is frequently very meagre indeed.

Not only are the data meagre, but frequently they are misleading. Thus, the results of analysis of a few scattering samples of sewage may do more harm than good, because they are not representative.

That sewage possesses a wide variation, both in quality and in quantity, at different hours of the day is, of course, very well known. In order to illustrate fully the significance of this to one who has to deal with the results of analyses of a few scattering samples, Table I is given. It shows the percentages which the volume of flow and the amount of the principal constituents of sewage at different hours of the day are of the average quantities. This table is computed from data given for the sewage purification works at Gardner in the Massachusetts State Board of Health Report for 1898, p. 624.

TABLE I.

COMPARISON OF THE PERCENTAGES WHICH THE FLOW OF SEWAGE AND THE AMOUNT OF ITS DIFFERENT CONSTITUENTS AT DIFFERENT HOURS ARE OF THE AVERAGES FOR THE DAY.

Hour.	Rate of Flow.	Residue on Evaporation.			Nitrogen as		Oxygen Consumed.	Chlorine.
		Total.	Dissolved.	Suspended.	Free Ammonia.	Albuminoid Ammonia.		
9-10 A.M.	124	143	126	180	150	180	158	99
11-12 "	116	160	159	162	157	155	167	114
1- 2 P.M.	123	129	131	125	107	107	110	127
3- 4 "	116	142	114	204	113	141	141	120
5- 6 "	107	123	137	93	116	99	92	217
7- 8 "	103	97	105	79	141	117	110	116
9-10 "	92	67	76	49	84	66	85	75
11-12 "	85	84	76	101	98	87	99	77
1- 2 A.M.	74	35	43	16	35	31	22	53
3- 4 "	70	28	39	6	8	15	16	38
5- 6 "	77	32	44	8	16	14	19	38
7- 8 "	114	69	74	59	101	87	82	61

The dangers of attaching too much significance to the results of limited data as to volume and strength of sewage have long been appreciated, and years ago resulted in the custom of rating the capacity of irrigation farms and intermittent sand filters according to the

population connected with the sewers per unit area of filtering surface. This was no doubt a wise custom, and it has served a useful purpose. But it has its limitations, owing to the fact that the amounts of some of the constituents of sewage are somewhat independent of the numbers of the contributing population, due especially to variations in quantity and quality of manufacturing wastes and of street washings which may be discharged into the sewers. Such limitations, of course, do not apply directly to residential and commercial communities which have separate sewers for the removal of storm water.

An endeavor has been made by the writer to gather together the available information as to the composition of sewage, partly with the view to securing data which would be of general assistance in connection with various problems in sewage disposal, and partly with the view to seeing wherein further studies are necessary in order to supplement data which are inadequate for allowing general deductions to be safely made.

The data herein compiled are somewhat fragmentary, and represent studies which have been made at odd times for several years of the available published records from sources with which the writer is more or less personally familiar. Acknowledgment is due here to the assistance of Mr. George A. Johnson, who has carefully reviewed the leading literature on the subject and compiled the various analyses in convenient form for use.

The composition of sewage representing different conditions can best be recorded by reducing the results of analyses and the gaugings of sewage flow to the common basis of the amount of the various constituents per capita per day. The data herein presented comprise, first, the published records of the amount of these constituents per capita, so far as they are known to the writer; and, second, the results which have been computed from the numerous analyses which in the last few years have been made and published in Massachusetts and in England.

The first records of which we have knowledge, showing the amount of the chief constituents of sewage per capita per day, are found in the notes and lectures by the late Dr. Letheby, which are reprinted in a book (p. 137) called "The Sewage Question," published in London in 1872 by Balliere, Tyndall & Cox. These results are the averages obtained from a great number of analyses by Dr. Letheby of the sewage discharged at all hours and at all seasons from the out-

falls of ten of the large London City sewers, whose ordinary rate of flow at midday was about five million gallons per day. These results are in close accord with those obtained in 1857 by Dr. Hoffman and Mr. Witt in their inquiries into the average composition of London sewage, and whose samples were taken hourly during the full twenty-four hours from the Savoy Street sewer, and mixed to produce fair average samples. Almost identical results were also obtained by Mr. Way in analyses of the Rugby sewage as the result of ninety-three analyses made from 1861 to 1863. Dr. Voelcker's estimate of the average composition is a little lower in some respects than that given by Dr. Letheby.

TABLE II.

DR. LETHEBY'S ESTIMATE OF THE AVERAGE AMOUNT OF THE PRINCIPAL CONSTITUENTS OF CITY SEWAGE EXPRESSED IN GRAMS PER CAPITA DAILY.

		TOTAL.	FROM EXCRETA.	FROM OTHER REFUSE.
Organic nitrogen	total,	15.1	10.1	5.0
	dissolved,	13.2	0.1	4.1
	suspended,	1.9	1.0	0.9
Dissolved matters	total,	136.0	43.0	93.0
	mineral,	98.5	10.0	88.5
	organic and volatile,	37.5	33.0	4.5
Suspended matters	total,	93.0	19.0	74.0
	mineral,	53.5	3.0	50.5
	organic and volatile,	39.5	16.0	23.5
Total solids	total,	229.0	62.0	167.0
	mineral,	152.0	13.0	139.0
	organic and volatile,	77.0	49.0	28.0
Phosphoric acid	total,	43.0	24.0	1.9
	dissolved,	2.1	1.4	0.7
	suspended,	2.2	1.0	1.2
Potash	total,	3.2	1.9	1.3
	dissolved,	3.0	1.5	1.5
	suspended,	0.2	0.4	—

One of the most interesting features of this table is the estimate of the relative amounts of the several constituents coming from excreta and from other sources.

In the above table it is to be noted that the organic matter is not recorded in the form of nitrogen as ammonias or of oxygen consumed, but that it is indicated only as a total quantity, doubtless obtained by the loss on ignition of the residue on evaporation, presumably including some volatile matter. However, it is of interest and important to note that the total nitrogen is given, presumably obtained by

a combustion process, and indicating that about one-fifth of the organic matter as recorded represents nitrogen.

In the special report on the examination of water supplies by the Massachusetts State Board of Health of 1890, p. 788, Mr. F. P. Stearns, then chief engineer of the board, estimated the leading constituents of sewage per capita daily, based upon analyses of the London sewage during the years 1883 and 1884, the Lawrence analyses as then available and a few analyses from Worcester, Mass., to be as follows:

TABLE III.

MR. STEARNS' ESTIMATE OF THE AVERAGE AMOUNT OF THE PRINCIPAL CONSTITUENTS OF SEWAGE EXPRESSED IN GRAMS PER CAPITA DAILY.

Nitrogen	as free ammonia,	5.6
	as albuminoid ammonia,	1.1
	total,[1]	8.9
Dissolved solids,		99.0
Chlorine,		19.0

[1] This is added by the writer, and is taken as the sum of the nitrogen as free ammonia and three times the nitrogen as albuminoid ammonia.

The next published record of which we have knowledge concerning the amount of constituents of sewage per capita is found in Mr. Goodell's translation of Professor Baumeister's work on "The Cleaning and Sewerage of Cities," the German edition of which appeared in 1890 and the English edition in the spring of 1891. Professor Baumeister apparently made very careful inquiries into the volume of water used by the sixteen English cities from which samples of sewage were analyzed by the Royal Commission on River Pollution during the early 70's, and paid especial attention to the question of whether the population connected with the sewers corresponded to the number of persons used in figuring the results per capita. His results are given in Table IV for sixteen representative English cities and also for the city of London, although it is presumable that his data for London are less satisfactory in some respects than those recorded in Table II.

TABLE IV.

PROFESSOR BAUMEISTER'S ESTIMATE OF THE AVERAGE AMOUNTS OF THE PRINCIPAL CONSTITUENTS OF SEWAGE, EXPRESSED IN GRAMS PER CAPITA DAILY.

	LONDON.	AVERAGE OF SIXTEEN ENGLISH CITIES.
Nitrogen,	16	15
Dissolved matter,	129	127
Suspended matter { total,	112	79
Suspended matter { mineral,	71	43
Suspended matter { organic and volatile,	41	36
Total solids,	251	206

The next published records of the constituents of sewage per capita daily are found in the report of the Massachusetts State Board of Health for 1894, p. 474, where there is given an estimate from analyses, made under the charge of the writer, of the *fresh* sewage of Lawrence, the Worcester State Lunatic Hospital, Marlboro, Gardner and Framingham. The results are based on one set of analyses from each place, in which the sewage was collected hourly (with few exceptions), and gaugings made of the sewage at the same interval, thus allowing a representative analysis of the entire day's flow to be computed. No determinations were made of the total solids or of the matters in suspension.

There is considerable variation in the results obtained from the several places, due in part to difficulty in estimating the population upon the sewerage system. Connections had only been partially made at several of these places, and this required an estimate of the equivalent for a period of twenty-four hours of a considerable portion of the contributing population which worked in factories in the town and resided outside the district connected to the sewers. Another complication related to the relatively large volume of ground water which entered the outfall sewers. The constituents of this ground water had some connection with the contributing population, but for the most part it was believed to be independent thereof. In the results of the amount of constituents per capita, the ground water was disregarded, thus giving results which for this reason are perhaps a little too low. The average results of the five places mentioned are given below.

The remaining published record of the constituents of sewage per capita is given in the report of Mr. X. H. Goodnough, sanitary engineer, in the forthcoming report relative to the proposed Charles River

dam at Boston. It is based upon frequent analyses of sewage at Andover, Brockton, Marlboro and Spencer, Mass., and the quantity of nitrogen as albuminoid ammonia is estimated to be 1.02 grams per capita daily. The remaining constituents of sewage from these places are not given, as the albuminoid ammonia was used for a special purpose in connection with the permissible amount of pollution which streams may receive without offensive odor.

TABLE V.

ESTIMATE IN THE 1894 REPORT OF THE MASSACHUSETTS STATE BOARD OF HEALTH OF THE PRINCIPAL CONSTITUENTS OF SEWAGE, EXPRESSED IN GRAMS PER CAPITA DAILY.

Oxygen consumed	2 minutes' boiling,	13.50
	5 minutes' boiling,	19.80
Nitrogen as	free ammonia,	6.40
	albuminoid ammonia,	2.25
	organic,	7.20
	total,	13.60
Chlorine,		16.00
Fats,		18.50
Bacteria,[1]		322.00

[1] Expressed as billions per capita daily.

Summarizing the results of published records of estimates of the amount of the chief constituents of sewage per capita daily, giving due weight to those data which are based upon the most numerous analyses, the following average may be obtained:

TABLE VI.

ESTIMATED APPROXIMATE AVERAGE AMOUNTS OF THE PRINCIPAL CONSTITUENTS OF SEWAGE, BASED ON FOREGOING DATA AND EXPRESSED IN GRAMS PER CAPITA DAILY.

Oxygen consumed	2 minutes' boiling,	15.0
	5 minutes' boiling,	22.0
Nitrogen as	free ammonia,	7.0
	albuminoid ammonia,	2.5
	organic,	8.0
	total,	15.0
Chlorine,		19.0
Fats,		19.0
Dissolved matters	total,	136.0
	mineral,	99.0
	organic and volatile,	37.0
Suspended matters	total,	93.0
	mineral,	53.0
	organic and volatile,	40.0
Total solids,	total,	229.0
	mineral,	152.0
	organic and volatile,	77.0

The significance of the above data is not discussed until further evidence is presented, but there are several features which it is well to mention here, as follows:

This average is a composite result, and its several items do not specifically refer to the same sewage. For this reason the relative values are not as reliable as might be desired. The data of the last table represent in general the sewage from combined systems, due to the predominancy of English evidence, although the sewers in each of the Massachusetts cities studied in connection with Table V were designed, with the exception of those at Lawrence, on the separate system. The solids and suspended matters are based on London evidence, where there is a considerable amount of street washings during storms. The amount of manufacturing refuse in the sewage represented by the above data is comparatively small. As to the different forms of nitrogen in the organic matter, the total amount found in London is subdivided as indicated by the Massachusetts data of 1894, which, as stated, represent fairly fresh sewage. In fact, the dissolved oxygen was not exhausted in the samples as collected and analyzed, as will be seen by consulting the detailed data in the report mentioned.

One of the unfortunate features at present regarding data on the composition of sewage is the inadequateness with which analytical methods measure the capacity of the organic matter for consuming oxygen in connection with both filtration and dilution processes.

The old method of regarding the loss on ignition as organic matter is, of course, very crude, as the results also include quite a portion of volatile mineral matters, and, further, give no clue to the character of the organic material with reference to its power for consuming oxygen.

The amount of nitrogen in the form of the ammonias is more helpful, and is of much assistance in allowing comparisons to be made of purified sewage and of natural waters in which the organic matter is in a fairly stable condition. In raw sewage, however, the percentage of nitrogenous organic matter which appears in the form of the ammonias is quite variable, and depends upon a number of factors. Especially is this true of the nitrogen in the form of albuminoid ammonia as compared with the total organic nitrogen in raw sewage. This has led, in a few instances, to direct determinations of the nitrogen in the organic matter by means of the Kjeldahl process, a method

which, in the opinion of the writer, is worthy of a far wider adoption than it has met up to this time.

In connection with the carbonaceous matter, the oxygen consumed, or the oxygen absorbed, is a result which is obtained by a process that in some form or another has been applied since 1850. The number of modifications of the process, however, is so great that there is considerable difficulty in applying the results obtained at one laboratory to the conditions elsewhere, and in all cases the results indicate only a small fraction of the oxygen consumed under conditions in nature.

Illustrative of the varying relation of nitrogen in the form of albuminoid ammonia to the total organic nitrogen present in raw sewage, there is given below in Table VII the results of an experiment made in the Lawrence laboratory and published in the 1894 report of the Massachusetts State Board of Health, p. 461. A bottle of fresh sewage was analyzed just after its collection and again at frequent intervals, allowing the natural decomposition processes to take place at room temperature. In this table it is seen that fresh sewage contains dissolved oxygen, coming, of course, from the water supply which forms the principal portion of the sewage. It also contains nitrogen in the form of nitrates, as well as other salts which are completely oxidized. Through the agency of the bacteria and the oxygen dissolved in the water and yielded by the oxidized salts, the carbon of the organic matter is oxidized, and the organic nitrogen uniting with the hydrogen forms free ammonia.

Thus it is seen from the results in the table that the dissolved oxygen and the nitrates gradually disappear; the bacteria, for a time, increase; the oxygen consumed (carbonaceous matter) decreases; the nitrogen as free ammonia increases and the organic nitrogen (Kjeldahl) decreases. The nitrogen as albuminoid ammonia, however, remains approximately constant, notwithstanding that more than twenty parts of organic nitrogen are changed to free ammonia, and some five or six parts of free nitrogen escape into the atmosphere.

It is of interest in this connection to note that it is the soluble organic matter which is decomposed, and that there is comparatively little change in the suspended matter. Each day after the oxygen was exhausted there was a little air added during the mixing of the contents of the bottle to obtain a fair sample. Septic action took place, but not in the degree which would have been the case had the

TABLE VII.

CHANGES IN COMPOSITION OCCURRING IN FRESH LAWRENCE SEWAGE UPON STANDING IN A BOTTLE IN THE LABORATORY.
PARTS PER MILLION.

DATE OF EXAMINATION.		FREE AMMONIA.	NITROGEN AS							TOTAL NITROGEN.	OXYGEN CONSUMED.		PER CENT. OF DISSOLVED OXYGEN.	BACTERIA PER CUBIC CENTIMETER.
			ALBUMINOID AMMONIA.			ORGANIC. (BY KJELDAHL.)			NITRITES AND NITRATES.					
Day.	Hour.		Dissolved.	Suspended.	Total.	Dissolved.	Suspended.	Total.			Two Minutes.	Five Minutes.		
March 11	10.30 A.M.	18.5	5.8	2.1	7.9	31.4	9.1	40.3	3.5	62.2	85.0	132.0	57	1,190,000
" 11	12.30 P.M.	20.6	5.8	2.4	8.2	28.9	11.4	40.3	3.1	63.9	81.0	142.0	60	1,085,000
" 11	3.00 "	21.0	5.8	2.5	8.3	28.9	10.7	39.6	2.9	63.4	85.0	136.0	60	1,505,000
" 11	6.00 "	23.4	5.6	2.7	8.3	27.8	9.9	37.7	2.5	63.6	85.0	133.0	30	1,530,000
" 12	8.00 A.M.	40.7	4.9	3.9	8.8	11.6	12.2	23.8	0.3	64.6	74.0	107.0	0	20,475,000
" 12	12.00 M.	41.2	4.9	4.4	9.3	11.6	8.2	19.8	0.2	61.0	69.0	98.0	0	23,100,000
" 12	5.00 P.M.	41.2	4.2	4.2	8.4	11.6	10.1	21.7	0.0	62.7	69.0	98.0	0	20,000,000
" 13	10.30 A.M.	42.0	4.7	3.5	8.2	11.6	8.2	19.8	0.0	61.6	60.0	89.0	0	12,810,000
" 14	10.30 "	41.2	3.3	4.5	7.8	9.4	8.4	17.8	0.0	58.8	55.0	72.0	0	11,235,000
" 15	10.30 "	41.2	3.4	4.3	7.7	9.3	8.3	17.6	0.0	57.6	49.0	68.0	0	6,825,000
" 16	10.30 "	41.2	3.5	4.1	7.6	7.5	8.9	16.4	0.0	57.4	48.0	72.0	0	4,485,000
" 18	10.30 "	42.0	3.0	3.8	6.8	7.4	6.9	14.3	0.0	56.1	51.0	70.0	0	3,420,000
" 19	10.30 "	42.8	3.0	3.9	6.9	5.9	7.8	13.7	0.0	56.3	50.0	71.0	0	2,341,000

sewage first been seeded with a septic growth. This experiment suggests, however, that in large septic tanks the processes of decomposition and putrefaction may not be so rapid that a difference of a few hours in the period occupied by the flow of the sewage through the tank affects materially the soluble parts of the sewage passing through it. The physical aspect of the process should be considered, namely, that the velocity of flow should be reduced so that suspended matters may subside, and the tank should be large enough to retain suspended matters sufficiently long to allow solution of suspended organic matter to take place, and thus avoid cleaning the tank at too frequent intervals.

Table VIII shows some comparisons by percentage of the several amounts of the different forms of nitrogen as found at various intervals in the experiment last described.

TABLE VIII.

COMPARISON OF THE RELATIVE AMOUNTS OF NITROGEN IN DIFFERENT FORMS IN THE SEWAGE EXPERIMENTED WITH AS SHOWN IN TABLE VII.

DAY.	HOUR.	PERCENTAGE OF TOTAL NITROGEN FOUND AS				PERCENTAGE WHICH NITROGEN AS ALBUMINOID AMMONIA IS OF ORGANIC NITROGEN (KJELDAHL).
		ORGANIC NITROGEN. (KJELDAHL.)	ALBUMINOID AMMONIA.	FREE AMMONIA.	NITRITES AND NITRATES.	
March 11	10.30 A.M.	64	13	30	6.0	20
" 11	12.30 P.M.	63	13	32	5.0	20
" 11	3.00 "	62	13	33	5.0	21
" 11	6.00 "	59	13	37	4.0	22
" 12	8.00 A.M.	37	14	63	0.4	37
" 12	12.00 M.	32	15	67	0.3	47
" 12	5.00 P.M.	35	13	66	0.0	39
" 12	10.30 A.M.	32	13	68	0.0	41
" 14	10.30 "	30	14	74	0.0	44
" 15	10.30 "	31	13	72	0.0	44
" 16	10.30 "	29	13	72	0.0	46
" 18	10.30 "	25	12	75	0.0	48
" 19	10.30 "	24	12	76	0.0	50

The amount of organic nitrogen present in sewage was determined in early days by the combustion method. Later it was estimated

as twice the nitrogen in the form of albuminoid ammonia, and more recently it has been taken as three times. In preparing balance sheets recording the changes through which sewage passes when treated by various processes, particularly those preparatory to filtration, and including the septic process, it seems to the writer to be highly desirable to know more accurately about the relative changes in nitrogenous matter. Such data can hardly fail to add to our knowledge of these subjects, and it is quite possible that the amount of nitrogen in the form of free ammonia as compared with the total nitrogen present in partially purified sewage may serve a useful purpose in the control of some preparatory treatments.

An effort has been made to find a formula for converting nitrogen in the form of albuminoid ammonia into organic nitrogen, giving due recognition to the range of free ammonia present in the sewage. It has been found that fair results, as a rule, are obtained in a majority of cases of Massachusetts sewages by using the following formula:

$$\text{Organic nitrogen} = \frac{\text{12 times the square of the nitrogen as albuminoid ammonia}}{\text{nitrogen as free ammonia}}$$

In the case of sewages which are very dilute, or of partially treated sewages, this formula does not work well, as will be seen in the next table, where comparisons are shown of the amount of organic nitrogen as actually determined by the Kjeldahl process and as estimated by this formula. The data from the several Massachusetts cities are averages of several analyses as described in the reports of the State Board of Health for the respective years. The experiment recorded in Table VII is also included, as well as data from Manchester given by Sir Henry Roscoe in his testimony before the Royal Commission on Sewage Disposal, 1902, Vol. II, p. 214.

TABLE IX.

COMPARISON OF THE AMOUNTS OF NITROGEN IN SEVERAL FORMS FOUND IN VARIOUS SEWAGES, WITH REFERENCE TO THE RELATION BETWEEN ALBUMINOID AMMONIA AND ORGANIC NITROGEN BY THE KJELDAHL METHOD.

PARTS PER MILLION.

SOURCE OF SEWAGE.	DATE.	NITROGEN AS				PER CENT. WHICH NITROGEN AS ALBUMINOID AMMONIA IS OF	
		ORGANIC (KJELDAHL).		ALBUMINOID AMMONIA.	FREE AMMONIA.	ORGANIC NITROGEN.	FREE AMMONIA.
		Determined.	Estimated.				
Worcester, Hospital,	1894	32.5	68.00	5.9	6.1	18	97
Worcester, Hospital,	1895	32.5	47.00	5.5	7.7	17	72
Marlboro,	1894	24.8	46.00	10.7	30.1	43	36
Marlboro,	1894	12.6	15.50	5.0	19.4	39	26
Framingham,	1894	16.7	16.50	5.9	25.3	35	23
Framingham,	1895	14.5	14.10	4.3	15.7	30	27
Gardner,	1894	11.2	11.70	3.1	9.5	28	33
Lawrence (fresh sewage),	1894	18.5	15.60	4.4	14.9	24	30
Lawrence (fresh sewage),	1895	21.6	25.00	5.3	13.5	25	39
Lawrence (Station sewage),	1894	13.0	11.50	5.2	28.1	40	19
Lawrence (Station sewage),	1895	15.8	15.80	6.1	28.1	38	22
Lawrence sewage upon standing in bottle in laboratory. — 1st day,		39.5	38.80	8.2	20.9	21	39
Lawrence sewage upon standing in bottle in laboratory. — 2d and 3d days,		21.3	22.00	8.7	41.3	41	21
Lawrence sewage upon standing in bottle in laboratory. — 4th to 8th days,		16.0	15.80	7.4	41.7	46	18
Effluent of Ppt. tanks at Manchester, Eng., average of 6 analyses covering 2 weeks each. — 1st set,		6.1	2.30	2.0	21.2	33	9
Effluent of Ppt. tanks at Manchester, Eng., average of 6 analyses covering 2 weeks each. — 2d set,		5.3	1.35	1.4	17.5	26	8
Effluent of Ppt. tanks at Manchester, Eng., average of 6 analyses covering 2 weeks each. — 3d set,		5.1	1.04	1.3	19.5	25	7

It does not seem likely that a formula or a series of formulas can be developed which can equal in reliability the results obtained by actual determinations of the organic nitrogen by the Kjeldahl process. More information concerning organic nitrogen is certainly necessary, and it will be a simple matter later on to judge of the practicability of formulas for conversion.

Regarding the determination of oxygen consumed, it is the general custom in this country to make the determination by adding acid and

permanganate solution to the liquid, and heating the same for a period of five minutes before making a titration to obtain the result. In some places, as at Lawrence, it is customary to limit this period of boiling to two minutes. In Germany, however, the period of boiling is generally extended to ten minutes. In England, the temperature at which the liquid, after being treated with chemical solutions, is allowed to stand is 80° F., and the results are observed as to the oxygen consumed after periods of three minutes, fifteen minutes and four hours, respectively. It is readily seen that the results obtained and published from such a different number of methods are bound to be very variable, and to give rise to much confusion in making deductions from the evidence accumulated at various places.

It would be very desirable indeed if there could be determined the absolute amount of oxygen consumed, such as would indicate the total amount of oxygen necessary in order to oxidize crude organic matter completely. This is a point which apparently could be studied advantageously along lines which are indicated farther on.

Any of the methods for determining oxygen consumed, if carefully carried out, of course give data of assistance in connection with various problems, especially in estimating the degree of purification effected by a process. It is highly important, however, that the method by which oxygen consumed is obtained should be recorded in connection with all important reports and analyses. If this is done, it is possible within certain limits to convert the results obtained by any method into those which would be obtained by others.

Careful inquiry has been made in the endeavor to ascertain factors which might be used with moderate confidence for converting to an equivalent basis the results obtained from the various methods of estimating oxygen consumed. These factors, made up of many average comparisons, are given in the next table:

TABLE X.

APPROXIMATE COMPARISON OF AVERAGE AMOUNTS OF OXYGEN CONSUMED BY SEWAGE AND SEWAGE EFFLUENTS AS SHOWN BY DIFFERENT METHODS.

METHOD.	TEMPERATURE OF SOLUTION.	PERIOD OF CONTACT.	RELATIVE RESULTS.
Kübel, as practiced at Boston and generally in America,	Boiling.	5 minutes.	1.00
Kübel, as practiced at Lawrence, Mass.,	Boiling.	2 minutes.	0.65
Kübel, as practiced in Germany,[1]	Boiling.	10 minutes.	1.25
English official tests,	80° F.	3 minutes.	0.20
	80° F.	15 minutes.	0.35
	80° F.	4 hours.	0.60
"Absolute" oxygen consumed,	Boiling.	4 hours.	4.00

[1] German results generally refer to "permanganate consumed" (*oxidirbarkeit*) and should be divided by four to give oxygen consumed.

With regard to the data used in arriving at these factors, it may be said that these comparisons between the Boston and Lawrence methods are obtained from numerous published records of the Massachusetts State Board of Health. The comparisons of the Kübel method, after heating five minutes and ten minutes, respectively, are based upon very limited information which was obtained by the writer a number of years ago. Comparisons of the Kübel boiling method and the official English method at 80° F. are obtained from Blair's book on "Organic Analyses of Waters," and from comparisons made in the laboratory of Professor Kinnicutt, of Worcester, and communicated privately to the writer.

As to the absolute oxygen consumed, the evidence is very limited indeed, being confined to about half a dozen observations given by Blair, p. 49, and by Sir Henry Roscoe in his testimony before the Royal Commission on Sewage Disposal, Vol. II, p. 212.

Regarding the factors given in Table X, of course it must be clearly borne in mind that in most instances they are only rough approximations for the purposes of the immediate present. It is believed, however, that they may be of some assistance in making comparisons until more adequate and reliable data are available. The discrepancies in the data obtained at different places indicate that these factors should be carefully worked out for different kinds of sewage.

Concerning the available evidence on the composition of sewage with reference to ascertaining the amounts of leading constituents per capita daily, as shown by analyses published within the last few

years in Massachusetts and England, it is unfortunate that so many records have to be ignored. This is on account of the data not being representative for the full twenty-four hours daily, and also lacking in the determination of so many constituents; and on account of inability to establish, even roughly, the relation between samples of sewage analyzed and the corresponding population and the volume of sewage flow.

The towns and cities in Massachusetts from which samples of sewage have been collected and analyzed in a manner to serve present purposes include Framingham, Gardner, Marlboro, and Worcester.

Table XI shows the estimated average composition of the sewage of each of these places, based on several series of hourly or bi-hourly samples for the full twenty-four hours per day, with corresponding gaugings of the sewage flow. The details will be found in the reports of the Massachusetts State Board of Health for the year in which the respective series of samples were collected, the dates of collection of the several series of samples being as follows:

Framingham, Sept. 11, 1894; Oct. 30, 1895; and April 17, 1899.
Gardner, July 19–26, inclusive, 1898; Jan. 31–Feb. 3, inclusive, 1899.
Marlboro, Aug. 23–30, inclusive, 1898.
Worcester, Sept. 4–10, inclusive, 1895.

The estimate of the average volume of sewage per capita daily is based on the following number of persons connected with the several sewerage systems: Framingham, 6,000; Gardner, 2,500; Marlboro, 1,200; and Worcester, 90,000. Worcester sewers in 1895 were on the combined plan, and the sewage contains iron and acid from steel works. At the other places the sewers are on the separate plan, and, generally speaking, receive only domestic sewage.

TABLE XI.

AVERAGE ANALYSES OF REPRESENTATIVE SEWAGE FROM MASSACHUSETTS CITIES, WITH ESTIMATED CORRESPONDING VOLUME PER CAPITA DAILY. PARTS PER MILLION.

		City (Mass.).			
		Framingham.	Gardner.	Marlboro.	Worcester.
Average daily flow of sewage per capita,	U. S. gallons,	73.0	100.0	113.0	150.0
	Imp. gallons	63.0	83.0	95.0	125.0
	liters,	275.0	375.0	430.0	562.0
Oxygen consumed,[1]		62.0	34.0	20.0	78.0
Nitrogen as	free ammonia,	21.5	15.8	7.7	11.2
	albuminoid ammonia,	5.7	3.8	2.7	5.2
	organic,[2]	18.1	10.7	11.3	29.0
	total,	39.6	26.5	19.0	40.2
Chlorine,		64.0	30.0	47.0	63.0
Dissolved matters	total,	312.0	185.0	232.0	548.0
	mineral,	200.0	110.0	181.0	357.0
	organic and volatile,	112.0	75.0	51.0	191.0
Suspended matters	total,	289.0	102.0	68.0	360.0
	mineral,	63.0	27.0	15.0	178.0
	organic and volatile,	226.0	75.0	53.0	182.0
Total solids	total,	601.0	287.0	300.0	908.0
	mineral,	263.0	137.0	196.0	535.0
	organic and volatile,	338.0	150.0	104.0	373.0

[1] These results are obtained by boiling for five minutes.

[2] This is estimated by the formula already given.

Table XII contains the estimated average composition of sewages in certain European cities where the data are sufficiently numerous to serve present purposes of comparison. The estimates are based upon recorded analyses of sewage, as follows:

Huddersfield. — The average analysis of sewage in this manufacturing city (population about 100,000) is based upon the mean result of hourly samples collected for twenty-four consecutive hours on five different occasions averaged with the mean analysis of the sewage from August, 1898, to February, 1900. The serial analyses are recorded on pp. 14–18 of the report of Mr. K. F. Campbell, borough engineer, on "The Sewage Problem," dated May, 1900. The latter analyses are stated by Mr. Campbell in the report of the Royal Commission on Sewage Disposal, 1902, Vol. III, p. 449. The sewers are on the combined plan, and 29 per cent. of the dry weather flow is made up of trade refuse.

Leeds. — This analysis represents sewage from a manufacturing city (population about 430,000) and covers the period from November, 1898, to June, 1900, as given by Colonel Harding in his testimony

to the Royal Commission, 1902, Vol. II, p. 382. The sewers are on the combined plan, and contain much trade waste, especially iron liquor.

Leicester. — The average analysis from this city (population about 220,000) represents the results from mixed half-hourly samples taken one day a week for a period of about one year, September, 1898, to September, 1899, inclusive, as recorded in the report of the borough engineer, Mr. E. G. Mawbey, upon the experiments made at Leicester and also as given by him in his testimony before the Royal Commission, 1902, Vol. II, p. 440. The sewers are on the combined plan, here, and receive wastes from dye works and wool-scouring establishments.

London, Northern Outfall. — This average analysis refers to a population of about 3,250,000, and is estimated from records obtained at different periods during the past twenty years. The more recent ones were obtained from bi-hourly samples collected day and night and averaged each day, regardless of the volume of flow. The data include an average analysis for 1883, as reported by Mr. Dibdin, report of the Royal Commission, 1884; an average for the year 1893, as recorded by the late Mr. Santo Crimp in his text-book, p. 158; an average for the year 1894, as recorded by Mr. Dibdin in his paper before the Institution of Civil Engineers, Vol. CXXIX, p. 55; and the results obtained during the past five years, as reported by Professor Clowes in his testimony before the Royal Commission on Sewage Disposal, 1902, Vol. III, as follows: for the period from September, 1898, to April, 1899, p. 458; for the year 1900, on p. 375; and for the period of November, 1900, to August, 1901, on p. 419. The first set of analyses is the most complete, and the estimated average as recorded in Table XII shows some features which are based upon the conditions which governed for the year 1883. Ground water and manufacturing refuse do not seem to have been a very important factor at this place. The sewers are on the combined plan.

London, Southern Outfall. — This average result is based upon the data for the years 1893 and 1894, as given by Mr. Dibdin in the same reference as for the northern outfall, also the analyses recorded by Professor Clowes for the period from November, 1889, to July, 1900, given in his testimony before the Royal Commission, Vol. III, p. 455. These analyses represent a somewhat different sewage than that of the northern outfall, due in part to manufacturing refuse, but more particularly to ground water entering the outfall sewer along the

salt marshes on the way to the outfall at Crossness. The sewers are on the combined plan, and receive the sewage of about 1,675,000 people.

Manchester. — The average analysis of the sewage from this manufacturing city (population about 562,000) is based on hourly samples, which were mixed in equal proportions, from Monday noon until Friday noon, to give four representative daily samples per week. The data cover the period from May 16, 1900, to January 24, 1901, as found in Tables VII and VIII and on p. 37 of the Report of the River Department for the year ending March 27, 1901. Much trade refuse is received by the sewers, which are on the combined plan.

TABLE XII.

AVERAGE ANALYSES OF SEWAGE FROM ENGLISH CITIES, WITH ESTIMATED CORRESPONDING VOLUME PER CAPITA DAILY. PARTS PER MILLION.

		City.					
		Huddersfield.	Leeds.	Leicester.	London (North).	London (South).	Manchester.
Average daily flow of sewage per capita	U. S. gallons,	108.00	60.0	60.0	48.0	60.0	72
	Imp. gallons,	90.00	50.0	50.0	40.0	50.0	61
	liters,	410.00	225.0	225.0	180.0	225.0	275
Oxygen consumed	4 hours at 80° F.,	99.00	126.0	107.0	80.0	67.0	118
	5 minutes at 212° F.,	165.00	210.0	180.0	133.0	112.0	197
Nitrogen as	free ammonia,	10.70	23.6	—	39.0	34.5	24
	albuminoid ammonia,	6.05	11.3	14.2	4.3	4.3	6
Chlorine,		123.00	—	—	132.0	267.0	170
Dissolved matters	total,	715.00	1070.0	1045.0	870.0	1093.0	940
	mineral,	597.00	—	—	565.0	755.0	470
	organic and volatile,	118.00	—	—	305.0	338.0	470
Suspended matters	total,	346.00	610.0	635.0	483.0	408.0	370
	mineral,	164.00	240.0	—	228.0	183.0	200
	organic and volatile,	182.00	370.0	—	225.0	225.0	170
Total solids	total,	1061.00	1680.0	1680.0	1353.0	1501.0	1310
	mineral,	761.00	—	—	793.0	938.0	670
	organic and volatile,	300.00	—	—	560.0	563.0	640

In making estimates of the average composition of sewage from the foregoing data, it is necessary to divide them into classes according to the nature of the sewage, as follows: Domestic sewage (separate system) from the small Massachusetts cities; domestic sewage and street washings (combined system) from the metropolitan district of London; and the domestic sewage, street washings and trade wastes (combined system) from the several large manufacturing cities.

TABLE XIII.

QUANTITIES OF PRINCIPAL CONSTITUENTS IN GRAMS PER CAPITA DAILY OF SEWAGE OF VARIOUS CITIES CLASSED ACCORDING TO THE GENERAL NATURE OF THE SEWAGE.

		Domestic Sewage from Small Cities.				Domestic Sewage and Street Refuse from the Metropolitan District of London.			Domestic Sewage, Street Refuse and Trade Waste from Manufacturing Cities.					
		Framingham.	Gardner.	Marlboro.	Average.	North.	South.	Average.[1]	Huddersfield.	Leeds.	Leicester.	Manchester.	Worcester.	Average.
Oxygen consumed,		17.0	13.0	9.0	13.0	24.0	25.0	25	67.0	47.0	40.0	55.0	44.0	50.0
Nitrogen as	albuminoid ammonia,	1.6	1.4	1.2	1.4	0.8	1.0	1	2.5	2.5	3.2	1.7	2.9	2.5
	free ammonia,	5.9	5.9	3.3	5.0	7.0	7.8	8	4.4	5.3	—	6.7	6.3	5.5
	total,	—	—	—	9.7	—	—	13	—	—	—	—	—	—
Chlorine,		18.0	11.0	20.0	16.0	24.0	60.0	24	50.0	—	—	47.0	35.0	44.0
Dissolved matters	total,	86.0	69.0	100.0	85.0	157.0	248.0	157	294.0	240.0	236.0	260.0	308.0	268.0
	mineral,	55.0	41.0	78.0	58.0	102.0	172.0	102	245.0	—	—	130.0	201.0	178.0
	organic and volatile,	31.0	28.0	22.0	27.0	55.0	76.0	55	49.0	—	—	130.0	107.0	90.0
Suspended matters	total,	80.0	38.0	29.0	49.0	87.0	92.0	87	142.0	137.0	143.0	102.0	202.0	145.0
	mineral,	18.0	10.0	6.0	11.0	41.0	41.0	41	67.0	54.0	—	55.0	100.0	69.0
	organic and volatile,	62.0	28.0	23.0	38.0	46.0	51.0	46	75.0	83.0	—	47.0	102.0	76.0
Total solids	total,	166.0	107.0	129.0	134.0	244.0	340.0	244	436.0	377.0	379.0	362.0	510.0	413.0
	mineral,	73.0	51.0	84.0	69.0	143.0	213.0	143	312.0	—	—	185.0	301.0	247.0
	organic and volatile,	93.0	56.0	45.0	65.0	101.0	127.0	101	124.0	—	—	177.0	209.0	166.0

[1] The nitrogen is not an exact average, but is given in round numbers in partial conformity with the data of Dr. Letheby. See Table II.

Table XIII shows the individual data, with averages of the composition in grams per capita daily, of the sewage of the three classes above stated. These data are self-explanatory, except that it may be stated that the oxygen consumed in each case refers to the Kübel method and a five-minute period of boiling in accordance with the provisional conversion factor given in Table X. Regarding the London average, the chlorine and various amounts of solids are based on the records obtained at Barking (northern outfall) because they are more numerous than those available from Crossness (southern outfall), and also for the reason that the data from the latter are complicated as to chlorine and dissolved matters, due to the ground water entering the outfall sewer. The nitrogen results at London are rather lower than is expected from the data of Dr. Letheby, and for this reason the estimated average as stated is given in round figures. The total nitrogen in each average is an estimate, based somewhat, in the absence of actual data, upon general information.

It is true that the average data for the several classes of sewage as here presented are not based on as comprehensive knowledge of exact local conditions as is desirable, nor do they in every instance include the records from as many cities as is necessary to make them thoroughly representative. To persons of a precise turn of mind it is not difficult to point out inconsistencies and the lack of consideration of important features, and to inquire what specific influence is produced by different modes of living of the population considered; by different proportions of paved streets, by pavings of different kinds, and by the cleanliness with which the streets are kept; by the frequency and intensity of rainfall with especial reference to storm overflows in the trunk sewers; and by differences in the amount and character of waste products of various industries.

On the other hand, it is not to be forgotten that these estimated averages are ordinarily far safer guides than are results of many scattering analyses, as will be appreciated by comparing the range in quantities given in Table XIII for the several classes of sewage with that in Table I. Again, in considering sewage disposal problems it is the duty of the engineer and sanitarian to give due regard to the future, for which no specific individual data are available, and judgment must be based on well-digested generalizations from past experiences which are thoroughly understood.

Knowing approximately the number of persons connected to a

sewerage system and the average flow, which information within certain limits is essential for the proper design of the collecting sewers, it is feasible to estimate the average composition of the sewage from such data as given in Table XIII. For purposes of ready comparison it is convenient to prepare tables showing the composition of sewage, based on such averages and corresponding to different degrees of dilution. It is unnecessary to burden this paper with such voluminous tables, but it may be stated here that "grams per capita daily" give the same figures for the several constituents, corresponding to the different forms of expressing the analyses, when the volume of sewage in United States gallons per capita daily is as follows·

Parts per million . . .	264.0	gallons.
" " 100,000 . . .	26.4	"
Grains per U. S. gallon . .	15.4	"
" " Imperial gallon .	18.5	"

For some time the writer has used tables prepared from the data of Table XIII to show the estimated composition of sewage corresponding to a wide range in volume per capita, and has found them of much assistance.

Before dismissing the subject of the average composition of sewage it may not be amiss to mention that it is somewhat surprising to note how few data, which may be used for this purpose even with moderate safety, are available at this time, fifty years since systematic sewage analyses were begun. This is partly due to the fact that the majority of the many thousands of sewage analyses which have been made are not representative samples, nor are the individual conditions which they represent recorded in a manner to permit of their general use. It is also caused in part by the tendency of the past dozen years to make only partial analyses for the purpose of indicating quickly and frequently the degree of purification effected by purification processes under trial.

Regarding methods of sampling, it is gratifying to note that there has been much improvement during the past five years at various places. This is very important, as it is easy to obtain distorted data by poor sampling. Looking at Table I it is seen that a comparison of the strongest sewage with the weakest, even if no purification

process were employed, would show a high percentage of purification should such samples be collected to indicate the efficiency of a process, as is quite possible under some circumstances, especially if only partial analyses are made.

As to methods of analyses as regularly practiced, there have not been many important changes in thirty years. This has its advantages and disadvantages. The advantages relate to the comparableness of general data from the same laboratory, and have resulted in a large fund of information to assist in arriving at certain leading features in connection with purification processes. The disadvantages are that the analytical data are not sufficiently comprehensive to allow thorough study of many important details such as are necessary in considering this subject to its logical conclusions. In the opinion of the writer the time has come when it is much wiser to make fewer analyses and make them more complete, as well as having the samples more thoroughly representative, not only of sewage, but also of effluents. It is also important to see that the samples of sewage do not change materially in composition during the interval between collection and examination.

Returning to the three principles of sewage disposal stated in the first part of this paper, it may be said that in connection with the preparatory treatment of sewage preliminary to filtration, we need more data regarding both the quantity and quality of suspended matters in various classes of sewage. This refers especially to the organic matter and with especial reference to street refuse and mill wastes. The latter form a study by themselves, and in manufacturing cities should be studied separately from the domestic sewage so far as estimates of the composition of sewage are concerned, although the data in the last column of Table XIII are of general assistance. At present the relative amounts of organic matter in solution and in suspension in sewage, as they actually exist at purification works (not in the laboratory), are not well known, and no attempt in this paper has been made to estimate them, except so far as indicated by loss on ignition.

Regarding preparatory treatments for sewage, especially the septic process, and methods of filtration involving high rates with a degree of purification sufficient only to secure a stable effluent, it is believed that detailed studies of the changes in the organic matter similar to and extending beyond the special experiment outlined in Table VII

will advance our practical knowledge of these processes and lead to a more advantageous application of them. If the data in the table mentioned are representative, then it seems that albuminoid ammonia determinations are of far less value than the organic nitrogen by the Kjeldahl method, and possibly may be omitted with safety. Certainly they now do not seem to have sufficient value to be made to the exclusion of the Kjeldahl process. The future of the albuminoid ammonia determination, judged strictly on its merits, appears to depend on the practicability of conversion factors such as already noted on p. 146, when considered for sewage work. This remark does not apply to natural waters. It seems to the writer that the time is ripe for a thorough review and comparison of methods for determining organic matter in sewage on a scale as comprehensive as made in connection with natural waters under Professor Mallet for the National Board of Health over twenty years ago. To the thought of the writer, the future of sewage chemistry cannot depend upon the question of convenience of manipulation in the laboratory, or that of the degree of skill of laboratory assistants.

Concerning the disposal of sewage into streams and ponds, the statement was made by Dr. Letheby in 1867 that (English) sewage if diluted with at least twenty volumes of water will not only be made inoffensive, but will be thoroughly destroyed after flowing a dozen miles or so. In 1878 the River Pollution Commission of Great Britain concluded that no river in that country was long enough to allow a complete disappearance of sewage matter discharged into it. Mr. Rudolph Hering concluded in 1888 (see Proceedings for that year of American Public Health Association) that to render sewage inoffensive to communities situated on a stream below the point of discharge, so far as putrefaction is concerned, it is necessary to have a dilution of at least 2.5 to 3 cubic feet per second per thousand population connected to the sewerage system. In 1890, the Massachusetts State Board of Health published a report by Mr. Stearns upon this matter, in which he reviewed very carefully the Massachusetts evidence then available, and including an estimate of the average composition of sewage (see Table III). His conclusions were that a dilution of 2.5 cubic feet per second per thousand persons was the least permissible, and that under certain conditions it might be necessary to have 7 cubic feet in order to guard against offensiveness.

In England, several river boards have adopted the standard, independent of questions of infection, of 1 grain of oxygen absorbed (4 hours at 80° F.) per Imperial gallon for the purity of sewage effluents discharged into relatively very small water courses. The practicability of this standard has been exploited by means of the so-called incubator test, which throws much light upon the biological and chemical aspects of this matter of non-putrescible water.

From these and other studies of an engineering, chemical, and biological nature, fairly satisfactory general rules may be drawn regarding the amount of organic matter which may be safely discharged into streams. But for certain specific cases the data are not as definite as desired, and, as stated by Mr. Freeman in his report to the Charles River dam committee, it was necessary to make further studies in order to learn "just where to draw the line in avoiding unnecessary expense." The reports made to him by Mr. Goodnough, Mr. Clark, and Dr. Field were of much assistance, and it would be advantageous if they were continued and made to cover a wider range of conditions.

In studying exhaustively the chemical and biological changes which take place in polluted waters, and the conditions under which putrefaction may be avoided, it is believed that the relative significance should be studied of the "absolute oxygen-consuming powers" of the organic matter in sewage or effluent expressed in terms which can be readily appreciated; of the oxygen dissolved in the sewage or effluent, together with that which may be yielded by nitrates, sulphates, and other constituents of the liquid; of the oxygen similarly contained in the water into which the sewage or effluent is discharged; of the oxygen which may be received in the water by means of aëration and from higher forms of vegetable life; and of the absolute oxygen-consuming powers of the organic matter in the water of the stream and in the sediment on the bottom and sides of the stream itself. To these factors should be added the effect of the very important items of temperature and the period of time during which biological changes may take place.

The above paragraphs may give the impression that they are written without due appreciation of the difficulties involved in applying the suggestions made, and of the advance in knowledge resulting from chemical and biological studies as they have been made in the past ten years. Such an impression is not correct, as the difficulties

attending the study of such a complex subject are realized. While it is not feasible to develop laws of mathematical precision, it is believed that it is possible to obtain more definite knowledge of various factors under various known conditions. As to the part played by analytical data in the development of matters of sewage disposal, their value has unquestionably been great. In the opinion of the writer, however, methods employed for studying the composition of sewage in its various phases have fallen somewhat into a rut. It seems questionable whether the amount of added knowledge which may be obtained from a continuance of present methods year after year is going to be commensurate with the cost. In fact, it seems that the time is approaching when it is worth while to consider a recasting of the program for sewage analyses. This may be thought to be unwise because future data would not be comparable with the past. This objection is readily met by stating that there should be omitted in the future no determination of value. In fact, it is more complete data which are now needed. Samples for analysis should be more representative and should be freer of the influences of changes between collection and examination. Partial analyses should not refer to certain of the regular tests, but be supplementary to full analyses, and with new methods cover special points as they arise. By such a program, even if necessary to reduce the cost of work done, it is believed that practical knowledge of the composition of sewage can be placed on a more substantial basis.

BOOK REVIEWS.

Analytical Chemistry.[1]

American chemists and students of chemistry will welcome Mr. Hall's translation of Dr. Treadwell's work on qualitative analysis, for a most excellent book has been rendered into good English, and the clearness and precision of the original are fully preserved in the translation. The fact that the first German edition was exhausted within two years from its issue speaks well for the reception which it has met in that country, and it seems quite certain that its American critics will be obliged to confine themselves mainly to a simple review.

The first thirty-five pages of the book are devoted to "General Principles," and contain sections on oxidation, reduction, chemical mass action, ionization, hydrolysis, blowpipe and bead reactions, and reagents. The explanations of oxidation and reduction are beautifully simple, and the illustrative reactions are well chosen and comprehensive. The chemical method is used, while some chemists might perhaps prefer the more modern method of considering oxidation and reduction a simple addition or subtraction of electrical charges. The chapters on chemical mass action and the ion theory of Arrhenius, as well as the application of both to the question of hydrolysis and indicators, is so simply stated that only the dullest of students can fail of comprehension. The strength of reagents recommended is based upon the idea of equivalents; twice normal, normal, and half normal solutions are used, so far as possible, in the hope that the student will carry along the idea of quantity as well as kind throughout the analysis.

The following two sections, "Reactions of the Cathions," and "Anions," occupy 328 pages. Here will be found the chief value of the book as a work of reference, for the properties and reactions of the

[1] Treadwell, F. P. Analytical Chemistry. Translated from the second German edition by William T. Hall. Volume I. Qualitative Analysis. New York: John Wiley & Sons. $3.00.

metals and the metalloids are gathered together for the purpose of the analyst in a manner that is unsurpassed. Italics are frequently but not excessively used. Structural formulas are most clearly drawn, and must form an important element in the instruction. No attempt is made to make the method of instruction hinge entirely upon modern physical chemistry, but the important deductions from the theory of dissociation and the action of mass are frequently pointed out and their application explained. Reversible reactions are frequently exemplified and methods of overcoming the difficulties arising therefrom in analysis made clear. Altogether, these sections of the book cannot be praised too highly, and the reviewer knows of no book to which he would rather refer students for the properties and reactions of the ions.

The section on "Course of Analysis," containing forty pages, is undoubtedly the one upon which the greatest difference of opinion will arise among chemists. It is unusually full and complete, omitting little but the rare-earths. It seems, however, to be rather complicated and somewhat disconnected, and it is doubtful if the almost complete course of blowpipe analysis, which is required in the examination preliminary to the regular analysis, will meet with general approval. Bunsen's classifications for acids is used. The tables for the common metals present no unusual feature.

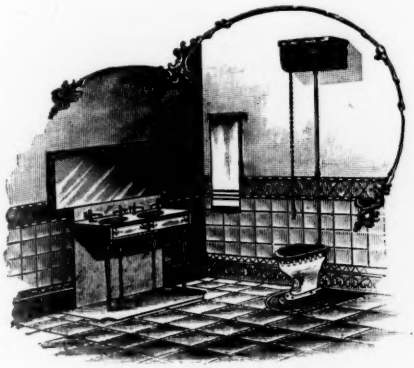
The supplement of fifty pages, upon the "Reactions of some of the Rarer Metals," is of decided importance, and is simply a continuance of the section on "The Reactions of the Metals" and of much the same character. Some of the metals have group separations outlined for them, but a general and simple scheme of analysis, which is so much needed, is not given.

A most excellent colored spectroscopic chart takes the place of a frontispiece.

As a whole the book is chiefly remarkable for the clearness, precision, and abundance of the subject-matter presented. No words are wasted. Americans will probably use the book more for reference in connection with some of our own excellent manuals than as a laboratory text-book. It should, however, be recommended to every student of qualitative analysis for his study desk.

The book is well indexed, and is clearly printed on good paper.

CHARLES LATHROP PARSONS.



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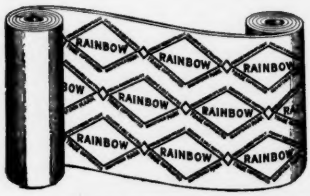

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